

Supporting Information

Enantioselective Synthesis of Planar-Chiral Benzosiloloferrocenes by Rh-Catalyzed Intramolecular C-H Silylation

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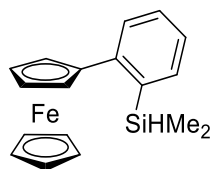
1) Experimental details and characterization data for new compounds

General information: ^1H NMR spectra were recorded on JEOL AL-500 (500 MHz) spectrometers. The chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) for CDCl_3 . The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, J , are reported in Hertz (Hz). ^{13}C NMR spectra were obtained by JEOL AL-400 (125 MHz) spectrometers and referenced to the internal solvent signals (central peak is 77.0 ppm in CDCl_3). CDCl_3 was used as a NMR solvent. High-resolution mass spectra (HRMS) were measured on a JMS-T100CS with ESI (Electro Spray Ionization) method. Optical rotations were measured on a JASCO DIP-1000 polarimeter. Preparative thin-layer chromatography (PTLC) was performed with silica gel-precoated glass plates (Merck 60 GF₂₅₄) prepared in our laboratory, Flash column chromatography was performed over silica gel 200-300. All reagents were weighed and handled in air and backfilled under Argon at room temperature. Unless otherwise noted, all reactions were performed under an argon atmosphere. All reagents were purchased from Wako, Kanto, Aldrich and TCI and used without further purification.

Typical experimental procedure for synthesis of 2-ferrocenyl-1-bromobenzene (Scheme 2): Water (55 ml), concentrated hydrochloric acid (8 ml) and 2-bromoaniline (0.58ml, 909 mg, 5.3 mmol) were added in a two necked flask, then a sodium nitrite solution in water (440 mg/ml, 8 ml, 6.36 mmol) was added dropwise by maintaining below $-5\text{ }^\circ\text{C}$. After 1 h, this mixed solution was warmed to room temperature, and was added sulfamic acid (779 mg, 6.5 mmol). A solution of ferrocene (1 g, 5.3 mmol) and NaOAc (800 mg, 9.75 mmol) in dichloromethane (60 ml) was added the above mixture. The solution was stirred for 12 h at room temperature. After the reaction was complete, the mixture was extracted with dichloromethane and washed by brine, water, and NaHCO_3 aq. The organic layer was dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The product was isolated by column chromatography on silica gel (hexane only) to give 2-ferrocenyl-1-bromobenzene (795 mg, 2.3 mmol, 44 %).

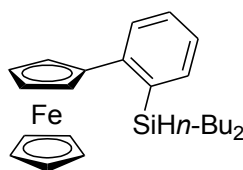
Typical experimental procedure for the synthesis of 2-ferrocenyl-1-(dimethylhydrosilyl)benzene (1aa) (Scheme 2): a solution of 2-ferrocenyl-1-bromobenzene (341 mg, 1 mmol) in THF (6 ml) was cooled to $-78\text{ }^\circ\text{C}$, and $n\text{-BuLi}$ (1.60 M in hexane, 1.9 ml, 3 mmol) was added dropwise under an atmosphere of argon. After 15 min, dimethylhydrochlorosilane (0.68 ml, 4 mmol) was added dropwise at $-78\text{ }^\circ\text{C}$ and mixture was warmed to room temperature slowly. After 12 h, a saturated solution of NH_4Cl in water was added and mixture extracted dichloromethane. The organic layer was dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The product was isolated by column chromatography on silica gel (hexane only) to give 2-ferrocenyl-1-(dimethylhydrosilyl)benzene (**1aa**) (256 mg, 0.8 mmol, 80 %yield).

Typical experimental procedure for enantioselective intramolecular silylation of 1aa: $[\text{Rh}(\text{coe})_2\text{Cl}]_2$ (3.6 mg, 0.005 mmol), chiral diene ligand (2.9 mg, 0.012 mmol), ferrocene **1aa** (16.0 mg, 0.05 mmol) and 3,3-dimethylbut-1-ene (64.6 μl , 0.5 mmol) were dissolved in toluene 0.5 ml. The resulting mixture was stirred at $135\text{ }^\circ\text{C}$. The progress of the reaction was monitored by TLC. After the reaction was complete, it was filtered through a short plug of silica gel with ethyl acetate and the filtrate was evaporated under reduced pressure. The crude products were purified by thin-layer chromatography (hexane) to give the mixture of **2aa** and **3aa**, whose ratio was determined by ^1H -NMR analysis. Compound **2aa** was separated from **3aa** by GPC (gel permeation chromatography) and was fully characterized.



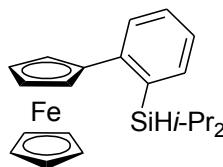
1-(Dimethylhydrosilyl)-2-ferrocenylbenzene (1aa).

Isolated by column chromatography (hexane only, $R_f = 0.5$). The title compound was obtained as orange solid (80%). Mp 89 °C, $^1\text{H NMR}$ δ 7.90 (dd, $J = 0.9, 3.8$ Hz, 1H), 7.47 (dd, $J = 0.9, 3.8$ Hz, 1H), 7.39 (ddd, $J = 1.3, 7.5, 8.2$ Hz, 1H), 7.24 (ddd, $J = 1.3, 7.5, 8.2$ Hz, 1H, overlap with CHCl_3), 4.44-4.55 (m, 3H), 4.27 (t, $J = 1.8$ Hz, 2H), 4.17 (s, 5H), 0.10 (d, $J = 3.7$ Hz, 6H); $^{13}\text{C NMR}$ δ 145.0, 136.6, 134.6, 131.1, 128.9, 125.7, 91.4, 70.5, 69.4, 67.7, -3.0. IR (CH_2Cl_2 cast film): 2359, 1749, 1216, 882, 417 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{18}\text{H}_{20}\text{FeSi}$ (M^+): 320.0678; found: 320.0678.



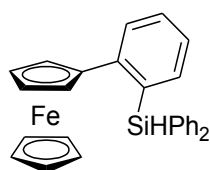
1-(Dibutylhydrosilyl)-2-ferrocenylbenzene (1ab).

Isolated by column chromatography (hexane only, $R_f = 0.4$). The title compound was obtained as orange oil (95%). $^1\text{H NMR}$ δ 7.90 (dd, $J = 1.1, 3.8$ Hz, 1H), 7.44 (dd, $J = 1.1, 3.8$ Hz, 1H), 7.38 (ddd, $J = 1.3, 7.5, 8.2$ Hz, 1H), 7.22 (ddd, $J = 1.3, 7.5, 8.2$ Hz, 1H), 4.44 (t, $J = 1.8$ Hz, 2H), 4.21-4.27 (m, 3H), 4.17 (s, 5H), 1.15-1.29 (m, 8H), 0.81 (t, $J = 7.0$ Hz, 6H), 0.54-0.67 (m, 4H); $^{13}\text{C NMR}$ δ 145.1, 135.4, 135.4, 131.2, 128.7, 125.9, 91.9, 70.8, 69.6, 67.8, 27.0, 26.2, 13.7, 12.1. IR (CH_2Cl_2 cast film): 2922, 2102, 1420, 816, 486 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{24}\text{H}_{32}\text{FeSi}$ (M^+): 404.1617; found: 404.1619.



1-(Diisopropylhydrosilyl)-2-ferrocenylbenzene (1ac).

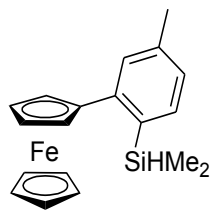
Isolated by column chromatography (hexane only, $R_f = 0.5$). The title compound was obtained as orange oil (80%). $^1\text{H NMR}$ δ 7.92 (d, $J = 7.16$ Hz, 1H), 7.41 (dd, $J = 7.37, 1.0$ Hz, 1H), 7.36 (ddd, $J = 7.60, 7.60, 1.5$ Hz, 1H), 7.21 (ddd, $J = 7.44, 7.44, 1.2$ Hz, 1H), 4.42 (t, $J = 1.77$ Hz, 2H), 4.24 (t, $J = 1.77$ Hz, 2H), 4.16 (s, 5H), 3.88 (t, $J = 3.6$ Hz, 1H), 1.02-1.07 (m, 2H), 0.97 (d, $J = 7.0$ Hz, 6H), 0.87 (d, $J = 7.0$ Hz, 6H); $^{13}\text{C NMR}$ δ 145.3, 135.8, 134.5, 131.4, 128.5, 125.3, 91.7, 71.0, 69.4, 67.5, 19.3, 19.1, 11.7. IR (CH_2Cl_2 cast film): 3095, 2938, 2861, 2359, 2137, 1460, 1420, 1002, 817; HRMS(ESI) calcd for $\text{C}_{22}\text{H}_{28}\text{FeSi}$ (M^+): 376.1304; found: 376.1304.



1-(Diphenylhydrosilyl)-2-ferrocenylbenzene (1ad).

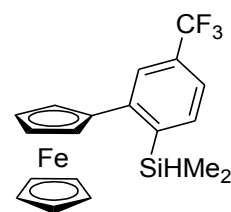
Isolated by column chromatography (hexane only, $R_f = 0.3$). The title compound was obtained as orange solid (88%). Mp 126 °C, $^1\text{H NMR}$ δ 7.94 (d, $J = 7.2$ Hz, 1H), 7.39-7.46 (m, 5H), 7.35-7.39 (m, 2H), 7.29-7.34 (m, 4H), 7.27 (dd, $J = 1.1, 7.5$ Hz, 1H), 7.16 (ddd, $J = 1.1, 4.0, 7.5$ Hz, 1H), 5.37 (s, 1H), 4.36 (t, $J = 1.8$ Hz, 2H), 4.11 (t, $J = 1.8$ Hz, 2H), 4.08 (s, 5H); $^{13}\text{C NMR}$ δ 146.3, 137.0, 135.8, 134.5, 132.0, 130.9,

129.4, 127.9, 125.5, 90.2, 70.5, 69.4, 67.8 (A pair of peaks at the aromatic rings was overlapped.). IR (CH₂Cl₂ cast film): 2922, 1770, 1375, 888, 648 cm⁻¹. HRMS(ESI) calcd for C₂₈H₂₄FeSi (M⁺): 444.0991; found: 444.0991.



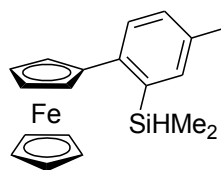
1-(Dimethylhydrosilyl)-2-ferrocenyl-4-methylbenzene (1ba).

Isolated by column chromatography (hexane only, R_f = 0.5). The title compound was obtained as orange oil (85%). ¹H NMR δ 7.72 (s, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 4.37-4.55 (m, 3H), 4.26 (s, 2H), 4.17 (s, 5H), 2.43 (s, 3H), 0.08 (s, 6H); ¹³C NMR δ 145.0, 138.6, 134.8, 133.1, 131.9, 126.7, 91.6, 70.5, 69.5, 67.7, 21.5, -2.9. IR (CH₂Cl₂ cast film): 2923, 2359, 1770, 1507, 1245 cm⁻¹. HRMS(ESI) calcd for C₁₉H₂₂FeSi (M⁺): 334.0835; found: 334.0834.



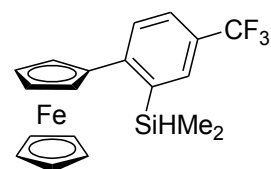
1-(Dimethylhydrosilyl)-2-ferrocenyl-4-(trifluoromethyl)benzene (1ca).

Isolated by column chromatography (hexane only, R_f = 0.5). The title compound was obtained as orange oil (79%). ¹H NMR δ 8.17 (s, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 4.42-4.57 (m, 3H), 4.30 (s, 2H), 4.17 (s, 5H), 0.12 (d, *J* = 3.7 Hz, 6H); ¹³C NMR δ 146.2, 141.3, 135.0, 130.8 (q, *J*_{C-F} = 31.9 Hz, 1C), 127.6 (q, *J*_{C-F} = 3.6 Hz, 1C), 124.3 (q, *J*_{C-F} = 271.5 Hz, 1C), 121.9 (q, *J*_{C-F} = 3.6 Hz, 1C), 90.2, 70.6, 69.6, 68.2, -3.3. IR (CH₂Cl₂ cast film): 2957, 2128, 1330, 1127, 880 cm⁻¹. HRMS(ESI) calcd for C₁₉H₁₉F₃FeSi (M⁺): 388.0552; found: 388.0552.



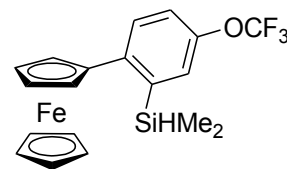
1-(Dimethylhydrosilyl)-2-ferrocenyl-5-methylbenzene (1da).

Isolated by column chromatography (hexane only, R_f = 0.5). The title compound was obtained as orange solid (66%). Mp 64 °C, ¹H NMR δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.26 (s, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 4.43-4.46 (m, 3H), 4.24 (t, 2H), 4.16 (s, 5H), 2.36 (s, 3H), 0.09 (d, *J* = 3.7 Hz, 6H); ¹³C NMR δ 141.9, 136.5, 135.3, 135.1, 131.1, 129.7, 91.4, 70.5, 69.4, 67.6, 21.1, -3.0. IR (CH₂Cl₂ cast film): 2994, 2954, 2115, 1758, 1246, 896; HRMS(ESI) calcd for C₁₉H₂₂FeSi (M⁺): 334.0835; found: 334.0834.



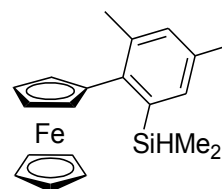
1-(Dimethylhydrosilyl)-2-ferrocenyl-5-(trifluoromethyl)benzene (1ea).

Isolated by column chromatography (hexane only, $R_f = 0.5$). The title compound was obtained as orange solid (89%). Mp 93 °C, $^1\text{H NMR}$ δ 7.98 (d, $J = 8.2$ Hz, 1H), 7.66 (s, 1H), 7.61 (d, $J = 8.2$ Hz, 1H), 4.50-4.53 (m, 3H), 4.32-4.33 (m, 2H), 4.17 (s, 5H), 0.14 (d, $J = 8.2$ Hz, 6H); $^{13}\text{C NMR}$ δ 149.4 (q, $J_{\text{C-F}} = 1.79$ Hz, 1C), 137.6, 131.2 (q, $J_{\text{C-F}} = 3.28$ Hz, 1C), 127.6 (q, $J_{\text{C-F}} = 31.6$ Hz, 1C), 125.5 (q, $J_{\text{C-F}} = 3.6$ Hz, 1C), 124.5 (q, $J_{\text{C-F}} = 271.8$ Hz, 1C), 89.8, 70.6, 69.7, 68.3, -3.2. IR (CH_2Cl_2 cast film): 3095, 2959, 2129, 1770, 1324, 1248, 1123, 1078, 889; HRMS(ESI) calcd for $\text{C}_{19}\text{H}_{19}\text{F}_3\text{FeSi}$ (M^+): 388.0552; found: 388.0552.



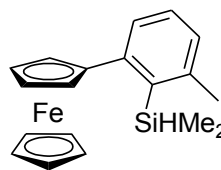
1-(Dimethylhydrosilyl)-2-ferrocenyl-5-(trifluoromethoxy)benzene (1fa).

Isolated by column chromatography (hexane only, $R_f = 0.5$). The title compound was obtained as orange oil (60%). $^1\text{H NMR}$ δ 7.91 (d, $J = 8.5$ Hz, 1H), 7.24 (s, 1H), 7.21 (d, $J = 8.5$ Hz, 1H), 4.45-4.48 (m, 3H), 4.28 (t, $J = 1.8$ Hz, 2H), 4.17 (s, 5H), 0.11 (s, 3H), 0.10 (s, 3H); $^{13}\text{C NMR}$ δ 147.3, 143.9, 139.2, 132.5, 126.6, 121.1, 120.6 (d, $J_{\text{C-F}} = 257.1$ Hz, 1C), 90.1, 70.5, 69.5, 68.0. IR (CH_2Cl_2 cast film): 3095, 2959, 2195, 1770, 1251, 1223, 886; HRMS(ESI) calcd for $\text{C}_{19}\text{H}_{19}\text{OF}_3\text{FeSi}$ (M^+): 404.0501; found: 404.0503.



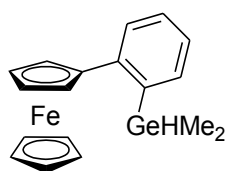
3,5-Dimethyl-1-(dimethylhydrosilyl)-2-ferrocenylbenzene (1ga).

Isolated by column chromatography (hexane only, $R_f = 0.4$). The title compound was obtained as orange solid (82%). Mp 88 °C, $^1\text{H NMR}$ δ 7.17 (s, 1H), 7.08 (s, 1H), 4.37-4.55 (m, 3H), 4.34 (s, 2H), 4.16 (s, 5H), 2.89 (s, 3H), 2.31 (s, 3H), 0.04 (d, $J = 3.7$ Hz, 6H); $^{13}\text{C NMR}$ δ 139.2, 139.1, 136.4, 135.1, 134.2, 133.1, 90.6, 70.9, 69.3, 67.5, 21.4, 20.9, -2.0. IR (CH_2Cl_2 cast film): 2951, 2116, 1248, 881, 489 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{20}\text{H}_{24}\text{FeSi}$ (M^+): 348.0991; found: 348.0991.



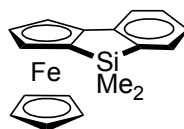
1-(Dimethylhydrosilyl)-2-ferrocenyl-6-methylbenzene (1ha).

Isolated by column chromatography (hexane only, $R_f = 0.4$). The title compound was obtained as orange oil (57%). $^1\text{H NMR}$ δ 7.80 (d, $J = 7.5$ Hz, 1H), 7.27 (t, $J = 7.5$ Hz, 1H), 7.07 (d, $J = 7.5$ Hz, 1H), 4.39 (t, $J = 1.8$ Hz, 2H), 4.21-4.29 (m, 3H), 4.16 (s, 5H), 2.48 (s, 3H), 0.14 (d, $J = 4.0$ Hz, 6H); $^{13}\text{C NMR}$ δ 145.4, 143.9, 136.3, 129.6, 128.3, 128.1, 93.7, 71.1, 69.4, 67.4, 23.5, -1.9. IR (CH_2Cl_2 cast film): 2360, 2125, 1770, 1246, 883 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{19}\text{H}_{22}\text{FeSi}$ (M^+): 334.0835; found: 334.0834.



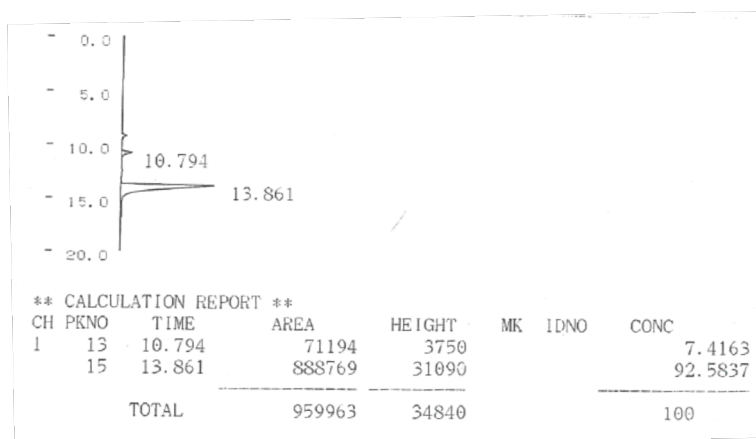
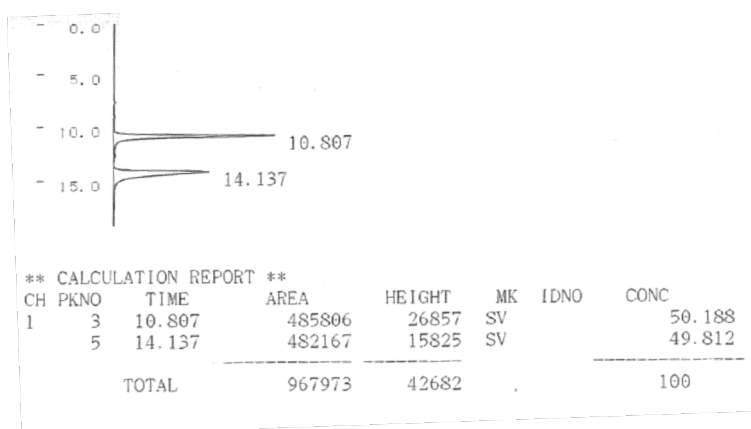
1-(Dimethylhydrogermyl)-2-ferrocenylbenzene(4).

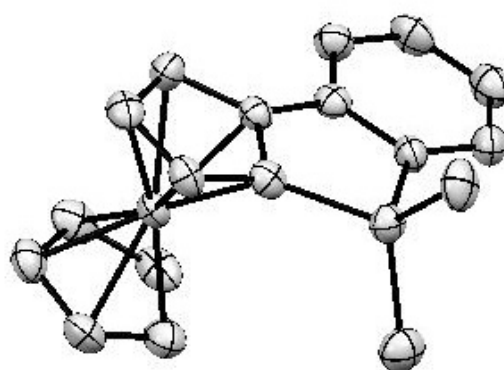
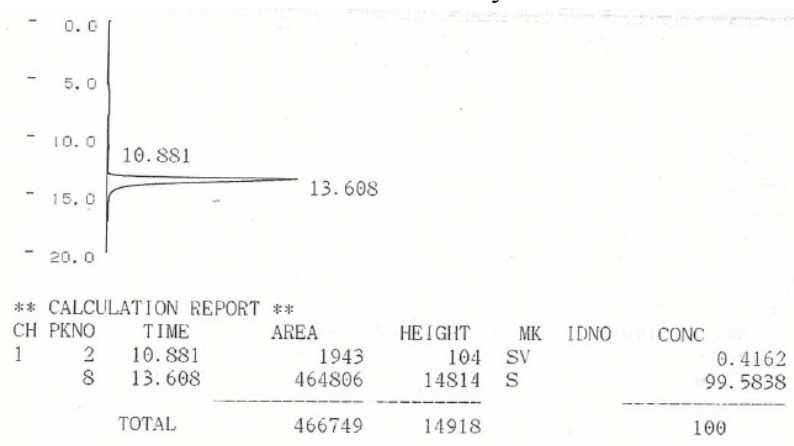
Isolated by column chromatography (hexane only, $R_f = 0.4$). The title compound was obtained as orange oil (10%). $^1\text{H NMR}$ δ 7.89 (d, $J = 7.6$ Hz, 1H), 7.31-7.44 (m, 2H), 7.18-7.26 (m, 1H, overlap with CHCl_3), 4.47-4.53 (m, 1H), 4.46 (t, $J = 1.8$ Hz, 2H), 4.26 (t, $J = 1.8$ Hz, 2H), 4.17 (s, 5H), 0.23 (d, $J = 3.4$ Hz, 6H); $^{13}\text{C NMR}$ δ 144.4, 139.1, 134.0, 131.0, 128.3, 125.9, 91.5, 70.4, 69.4, 67.7, -3.1. IR (CH_2Cl_2 cast film): 2923, 2855, 2358, 1456, 1246 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{18}\text{H}_{20}\text{FeGe}$ (M^+): 362.0153; found: 362.0151.



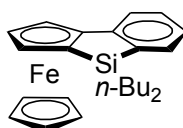
(S)-8,8-Dimethylbenzosilolo[2,3-a]ferrocene (2aa).

Isolated by thin-layer chromatography (hexane only, $R_f = 0.4$) and purified by gel permeation chromatography (GPC). The title compound was obtained as orange solid (81%). Mp 64 °C, $^1\text{H NMR}$ δ 7.42 (d, $J = 7.2$ Hz, 1H), 7.34 (d, $J = 7.5$ Hz, 1H), 7.26 (t, $J = 7.5$ Hz, 1H, overlap with CHCl_3), 7.12 (t, $J = 7.2$ Hz, 1H), 4.74-4.80 (m, 1H), 4.49-4.55 (m, 1H), 4.32-4.38 (m, 1H), 3.98 (s, 5H), 0.67 (s, 3H), 0.31 (s, 3H); $^{13}\text{C NMR}$ δ 147.8, 142.1, 132.4, 129.5, 125.2, 120.9, 97.0, 73.2, 71.7, 70.5, 69.7, 64.0, -0.8, -1.6. IR (CH_2Cl_2 cast film): 2924, 2361, 1742, 1363, 1216 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{FeSi}$ (M^+): 318.0522; found: 318.0521. $[\alpha]_D^{17} = -339$ (c 0.79, CHCl_3 , 85% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA-3: 4.6 x 250 mm, 254 nm UV detector, rt, eluent: hexane only, flow rate: 0.5 mL/min, retention time: 14.0 min for major isomer and 10.8 min for minor isomer). The crystal data of compound **2aa**: $\text{C}_{18}\text{H}_{18}\text{FeSi}$, $M = 318.27$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 9.6741(4)$ Å, $b = 10.9465(6)$ Å, $c = 29.0292(11)$ Å, $V = 3074.1(2)$ Å³, $Z = 8$, $\mu(\text{Mo-K}\alpha) = 10.447$ cm^{-1} ; number of reflections measured: total 29429 and unique 6966, $R_1 = 0.0371$, $wR_2 = 0.1036$, Flack parameter (Friedel pairs = 2036) 0.003(8). CCDC 1045375.

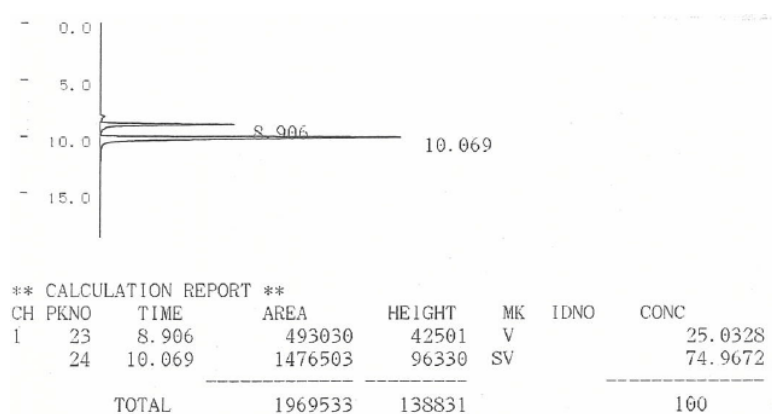
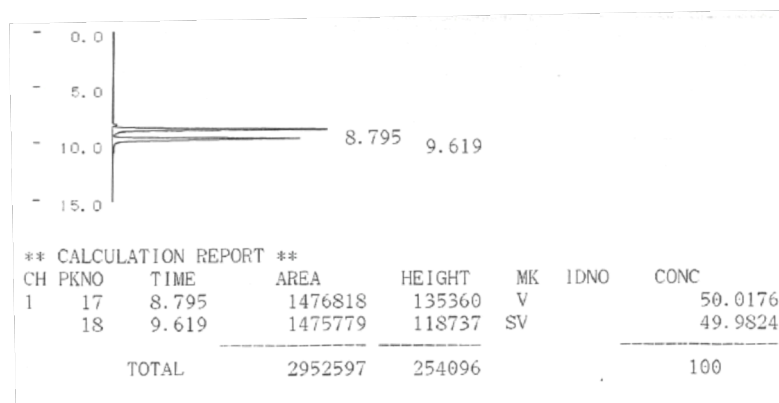


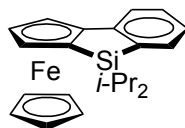
HPLC chart of **3aa** after recrystallizationORTEP diagram of (*S*)-**2aa**

8,8-Dibutylbenzosilolo[2,3-a]ferrocene (**2ab**).



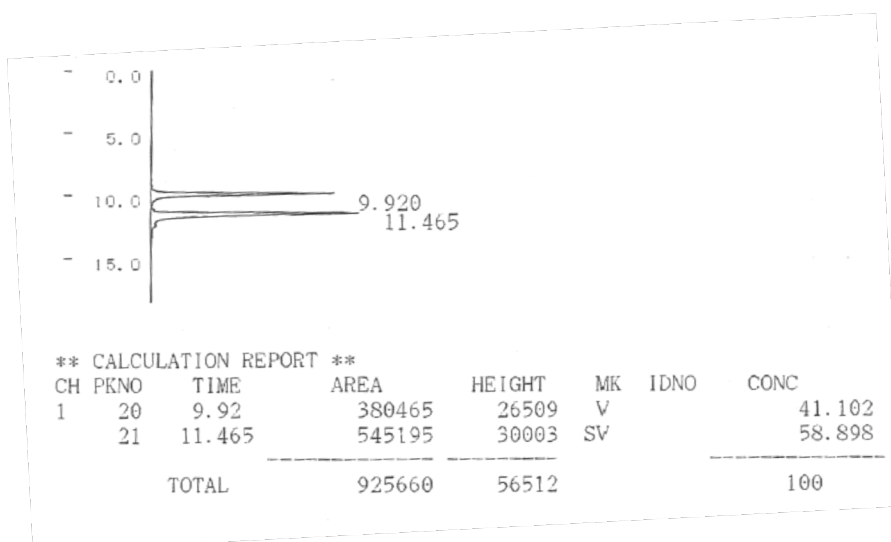
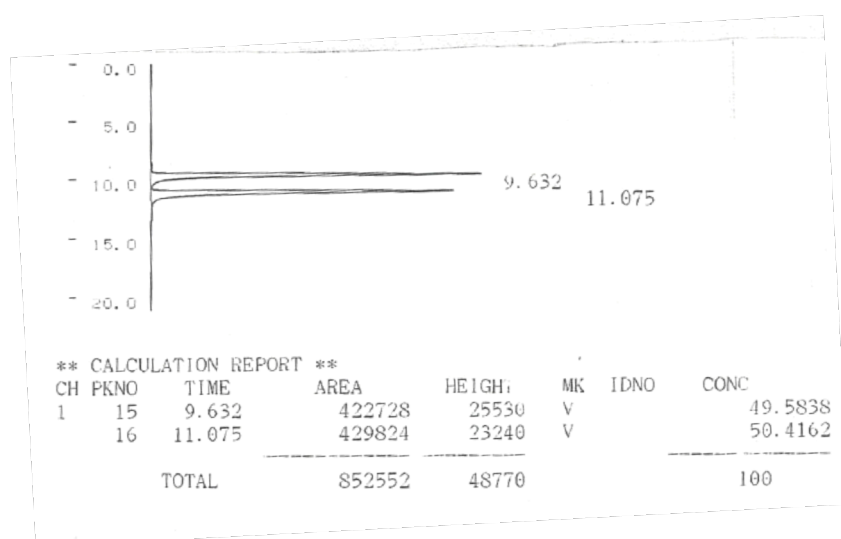
Isolated by thin-layer chromatography (hexane only, $R_f = 0.3$). The title compound was obtained as orange oil (51%). $^1\text{H NMR}$ δ 7.41 (d, $J = 7.0$ Hz, 1H), 7.34 (d, $J = 7.6$ Hz, 1H), 7.23-7.28 (m, 1H), 7.10 (ddd, $J = 0.9, 7.3, 8.4$ Hz, 1H), 4.77 (d, $J = 2.2$ Hz, 1H), 4.51 (t, $J = 2.2$ Hz, 1H), 4.30 (d, $J = 2.2$ Hz, 1H), 3.97 (s, 5H), 1.62-1.76 (m, 2H), 1.46-1.61 (m, 2H, overlapped with H_2O), 1.07-1.23 (m, 6H), 1.02 (t, $J = 7.3$ Hz, 3H), 0.70-0.83 (m, 5H); $^{13}\text{C NMR}$ δ 148.2, 141.0, 133.1, 129.4, 125.0, 121.0, 97.1, 73.1, 71.2, 70.1, 69.6, 63.9, 26.7, 26.6, 26.3, 26.2, 14.0, 13.7, 13.5, 13.4. IR (CH_2Cl_2 cast film): 2923, 2855, 2358, 1456, 1246 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{24}\text{H}_{30}\text{FeSi}$ (M^+): 402.1461; found: 402.1461. $[\alpha]_D^{22} = -98$ (c 0.51, CHCl_3 , 50% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA-3: 4.6 x 250 mm, 254 nm UV detector, rt, eluent: hexane only, flow rate: 0.5 mL/min, retention time: 9.8 min for major isomer and 8.9 min for minor isomer).

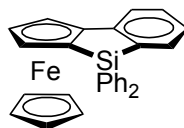




8,8-Diisopropylbenzosilolo[2,3-a]ferrocene (2ac).

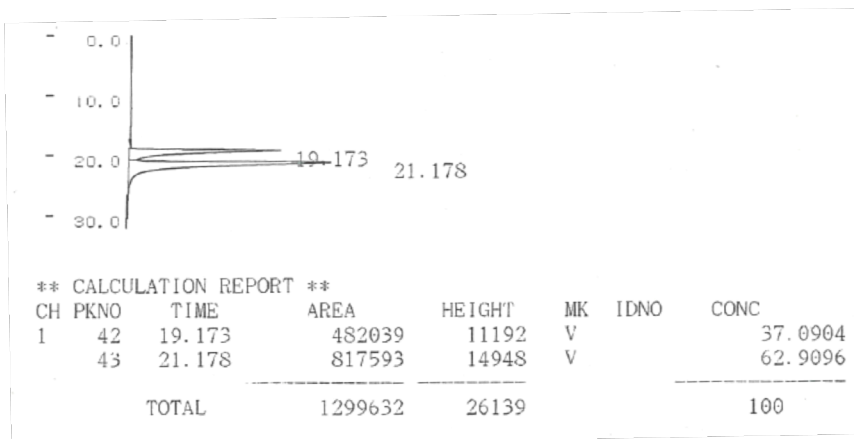
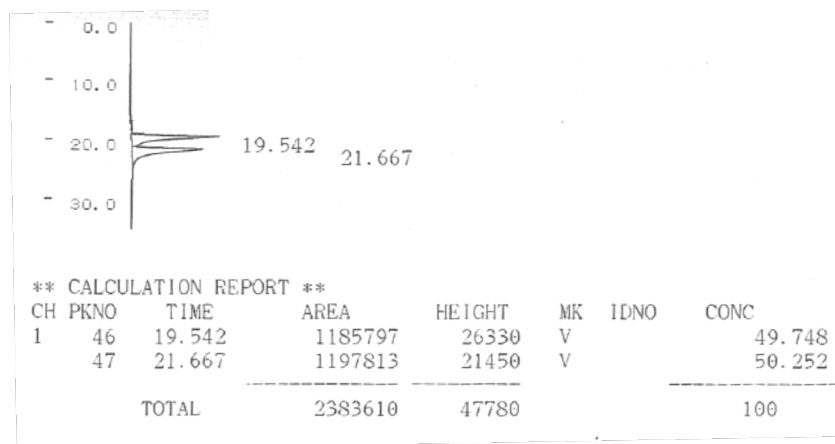
Isolated by thin-layer chromatography (hexane only, $R_f = 0.4$). The title compound was obtained as orange oil (39%). ^1H NMR δ 7.42-7.49 (m, 1H), 7.31-7.38 (m, 1H), 7.23-7.31 (m, 1H, overlapped with CHCl_3), 7.07-7.13 (m, 1H), 4.78 (d, $J = 2.2$ Hz, 1H), 4.53 (t, $J = 2.2$ Hz, 1H), 4.29 (d, $J = 2.2$ Hz, 1H), 3.98 (s, 5H), 1.46-1.53 (m, 1H), 1.43 (t, $J = 6.4$ Hz, 6H), 1.18-1.24 (m, 1H), 0.91 (d, $J = 7.3$ Hz, 3H), 0.82 (d, $J = 7.3$ Hz, 3H); ^{13}C NMR δ 148.5, 139.9, 133.4, 129.3, 125.0, 121.1, 97.2, 73.1, 71.0, 70.5, 69.7, 63.7, 18.9, 18.8, 18.7, 18.4, 14.0, 11.3. IR (CH_2Cl_2 cast film): 2924, 2359, 1749, 1350, 1229 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{22}\text{H}_{26}\text{FeSi}$ (M^+): 374.1148; found: 374.1148. $[\alpha]_D^{22} = -53$ (c 0.38, CHCl_3 , 18% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA-3: 4.6 x 250 mm, 254 nm UV detector, rt, eluent: hexane only, flow rate: 0.5 mL/min, retention time: 11.3 min for major isomer and 9.8 min for minor isomer).

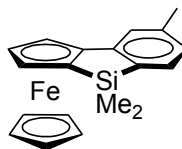




8,8-Diphenylbenzosilolo[2,3-a]ferrocene (2ad).

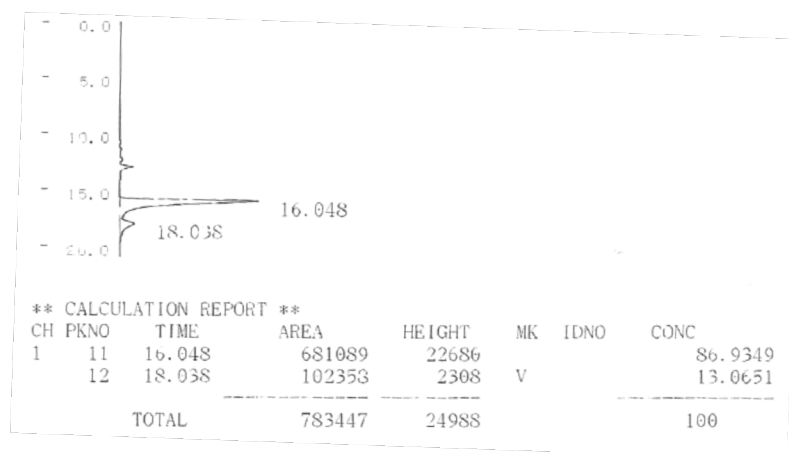
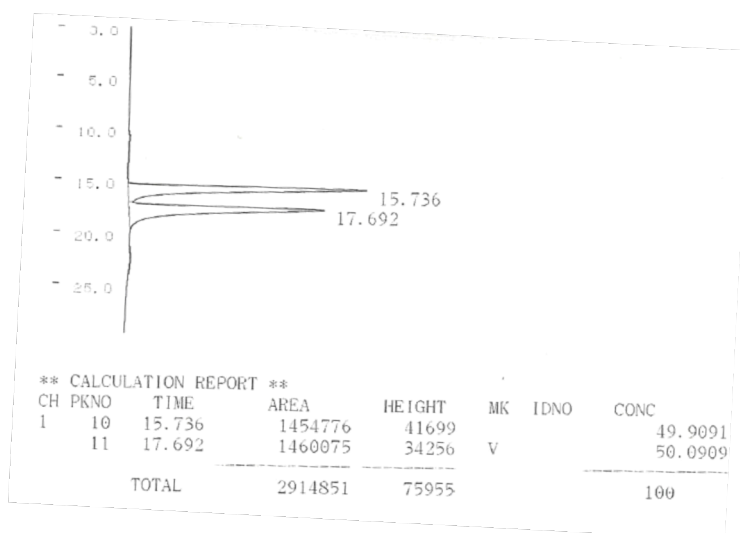
Isolated by thin-layer chromatography (hexane/EtOAc = 20/1, R_f = 0.5). The title compound was obtained as orange oil (74%). ¹H NMR δ 7.85-7.92 (m, 2H), 7.67 (d, *J* = 6.7 Hz, 1H), 7.47-7.52 (m, 4H), 7.46-7.47 (m, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.28-7.34 (m, 2H), 7.21-7.26 (m, 2H), 7.17-7.21 (m, 1H), 4.84 (d, *J* = 2.3 Hz, 1H), 4.60 (t, *J* = 2.3 Hz, 1H), 4.52 (d, *J* = 2.3 Hz, 1H), 3.65 (s, 5H); ¹³C NMR δ 148.9, 138.1, 135.8, 135.3, 135.3, 135.1, 134.5, 134.1, 130.1, 129.9, 129.6, 129.4, 128.1, 127.9, 127.8, 125.6, 121.3, 97.3, 73.7, 70.8, 70.1, 69.1, 64.3. IR (CH₂Cl₂ cast film): 2924, 2359, 1739, 1364, 698 cm⁻¹. HRMS(ESI) calcd for C₂₈H₂₂FeSi (M⁺): 442.0835; found: 442.0835. [α]²¹_D = -91 (c 0.82, CHCl₃, 26% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA-3: 4.6 x 250 mm, 254 nm UV detector, rt, eluent: hexane only, flow rate: 0.5 mL/min, retention time: 20.3 min for major isomer and 18.0 min for minor isomer).

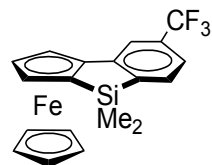




5,8,8-Trimethylbenzosilolo[2,3-a]ferrocene (2ba).

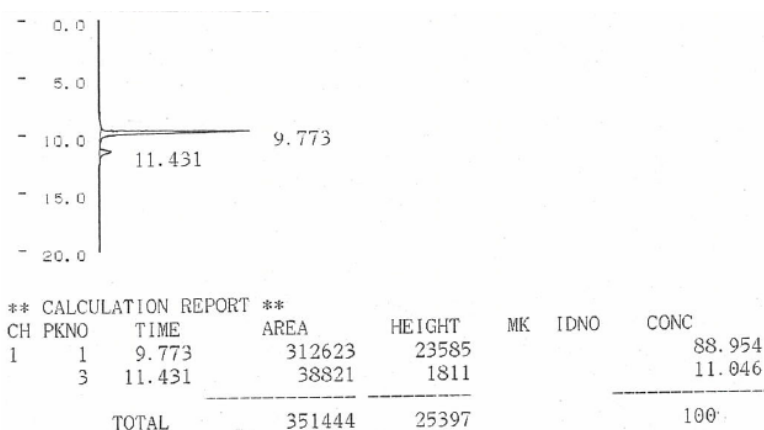
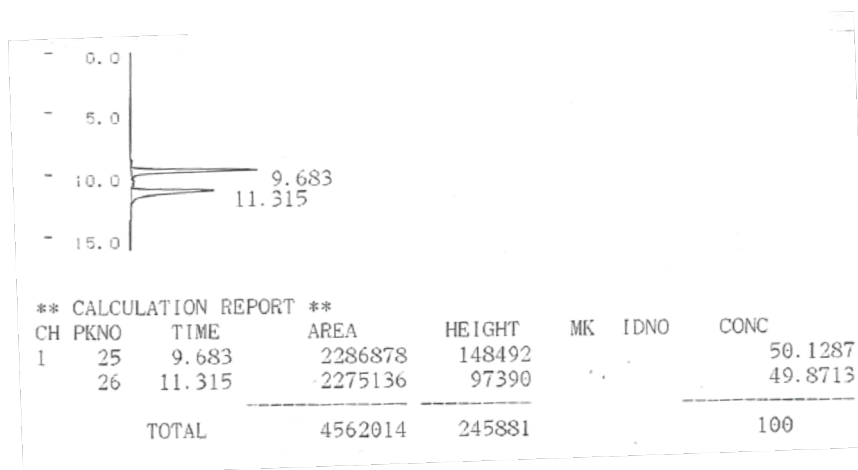
Isolated by thin-layer chromatography (hexane only, $R_f = 0.4$) and purified by gel permeation chromatography (GPC). The title compound was obtained as orange oil (56%). ^1H NMR δ 7.32 (d, $J = 7.3$ Hz, 1H), 7.17 (s, 1H), 6.95 (d, $J = 7.3$ Hz, 1H), 4.74 (d, $J = 2.2$ Hz, 1H), 4.50 (t, $J = 2.2$ Hz, 1H), 4.33 (d, $J = 2.2$ Hz, 1H), 3.98 (s, 5H), 2.35 (s, 3H), 0.65 (s, 3H), 0.29 (s, 3H); ^{13}C NMR δ 148.0, 139.3, 138.6, 132.3, 126.2, 121.8, 97.1, 73.0, 72.1, 70.4, 69.6, 63.9, 21.7, -0.7, -1.5. IR (CH_2Cl_2 cast film): 2922, 2321, 1244, 775, 418 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{19}\text{H}_{20}\text{FeSi}$ (M^+): 332.0678; found: 332.0677. $[\alpha]_{\text{D}}^{18} = -104$ (c 0.48, CHCl_3 , 74% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IF-3: 4.6 x 250 mm, 254 nm UV detector, rt, eluent: hexane only, flow rate: 0.5 mL/min, retention time: 15.9 min for major isomer and 17.9 min for minor isomer).

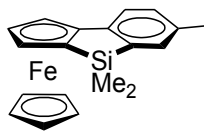




8,8-Dimethyl-5-(trifluoromethyl)benzosilolo[2,3-a]ferrocene (2ca).

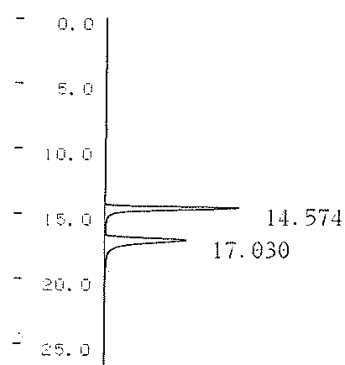
Isolated by thin-layer chromatography (hexane only, $R_f = 0.4$) and purified by gel permeation chromatography (GPC). The title compound was obtained as orange oil (55%). $^1\text{H NMR}$ δ 7.46-7.53 (m, 2H), 7.35 (d, $J = 7.5$ Hz, 1H), 4.82 (d, $J = 2.2$ Hz, 1H), 4.58 (t, $J = 2.2$ Hz, 1H), 4.40 (d, $J = 2.2$ Hz, 1H), 3.99 (s, 5H), 0.69 (s, 3H), 0.33 (s, 3H); $^{13}\text{C NMR}$ δ 149.1, 146.8, 132.6, 131.7 (q, $J = 31.8$ Hz, 1C), 124.5 (q, $J = 271.8$ Hz, 1C), 121.7 (q, $J = 3.7$ Hz, 1C), 116.9 (q, $J = 3.7$ Hz, 1C), 95.4, 73.8, 71.8, 71.0, 69.8, 64.4, -0.9, -1.8. IR (CH_2Cl_2 cast film): 2952, 1420, 1248, 837, 727 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{19}\text{H}_{17}\text{F}_3\text{FeSi}$ (M^+): 386.0396; found: 386.0396. $[\alpha]_D^{20} = -80$ (c 0.20, CHCl_3 , 78% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA-3: 4.6 x 250 mm, 254 nm UV detector, rt, eluent: hexane only, flow rate: 0.5 mL/min, retention time: 9.7 min for major isomer and 11.4 min for minor isomer).





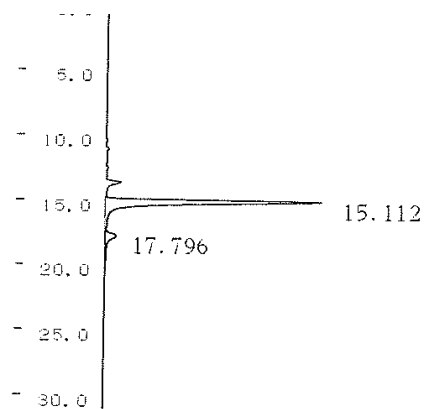
6,8,8-Trimethylbenzosilolo[2,3-a]ferrocene (2da).

Isolated by thin-layer chromatography (hexane only, $R_f = 0.45$) and purified by gel permeation chromatography (GPC). The title compound was obtained as orange oil (44%). ^1H NMR δ 7.23-7.24 (m, 2H), 7.06 (d, $J = 7.7$ Hz, 1H), 4.72 (d, $J = 2.1$ Hz, 1H), 4.88 (t, $J = 2.3$ Hz, 1H), 4.32 (d, $J = 2.1$ Hz, 1H), 3.97 (s, 5H), 2.31 (s, 3H), 0.66 (s, 3H), 0.30 (s, 3H); ^{13}C NMR δ 144.7, 142.2, 134.6, 133.3, 130.3, 120.7, 72.9, 71.5, 70.3, 69.8, 69.6, 63.8, 21.3, -0.7, -1.6. IR (CH_2Cl_2 cast film): 2996, 2359, 1770, 1245, 1056; HRMS(ESI) calcd for $\text{C}_{19}\text{H}_{20}\text{FeSi}$ (M^+): 332.0678; found: 332.0678. $[\alpha]_D^{23} = -245$ (c 0.32, CHCl_3 , 86% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IF-3: 4.6 x 250 mm, 254 nm UV detector, rt, eluent: hexane only, flow rate: 0.5 mL/min, retention time: 15.1 min for major isomer and 17.8 min for minor isomer).



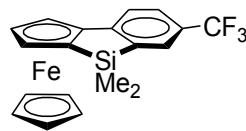
** CALCULATION REPORT **

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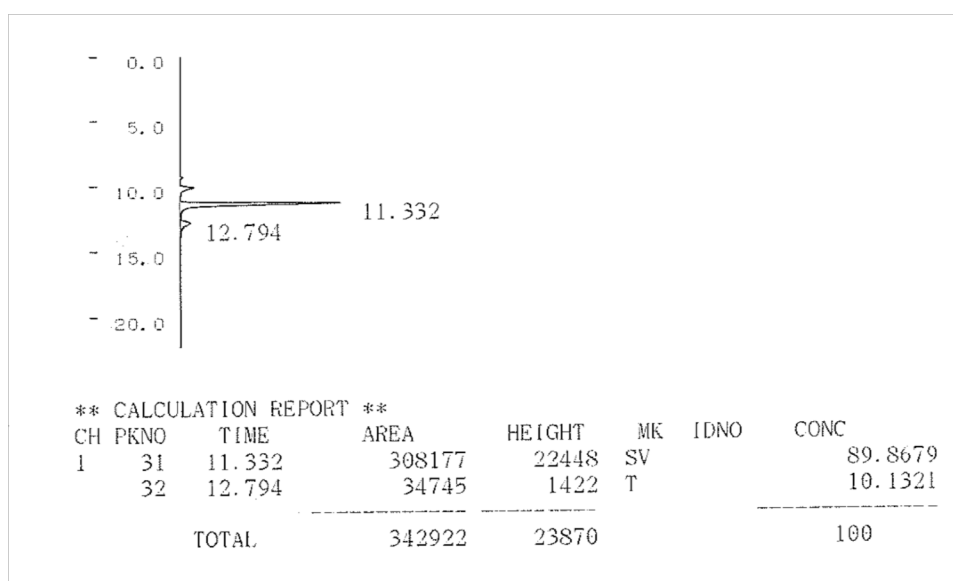
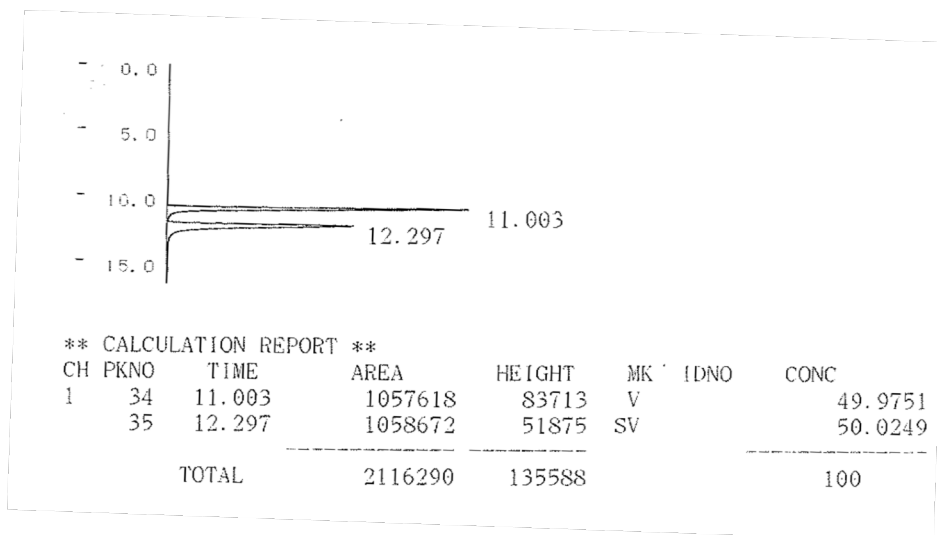
** CALCULATION REPORT **

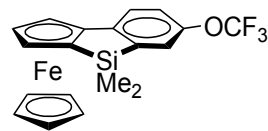
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1	32	15.112	344247	15110	SV		93.1464
	34	17.796	25329	737	T		6.8535
TOTAL			369576	15846			100



8,8-Dimethyl-6-(trifluoromethyl)benzosilolo[2,3-a]ferrocene (2ea).

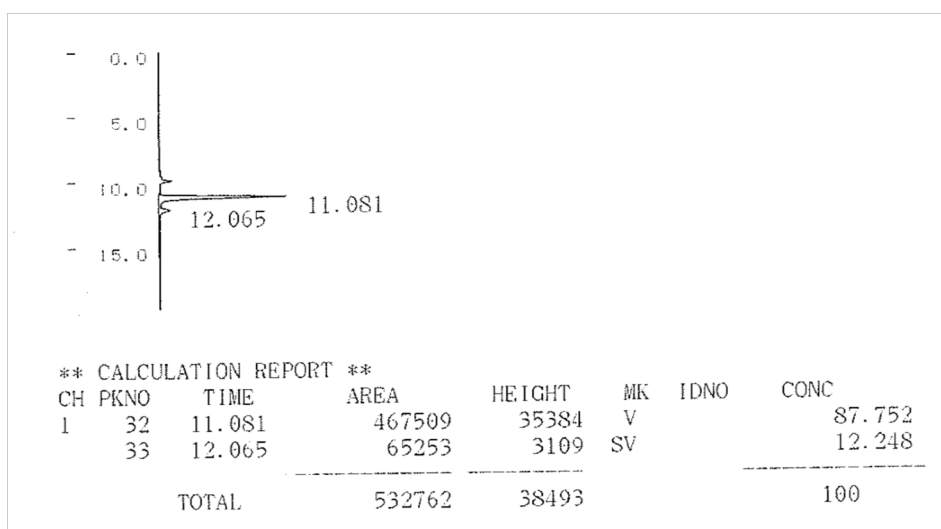
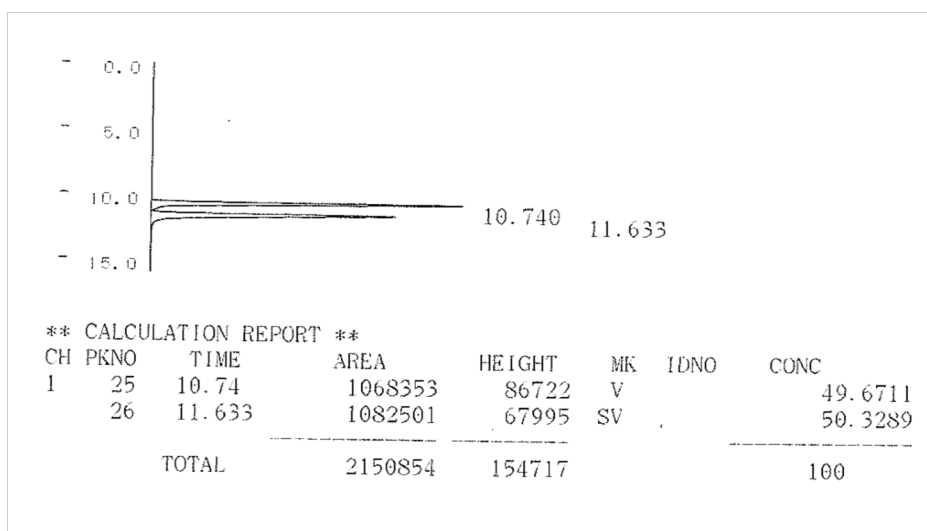
Isolated by thin-layer chromatography (hexane only, $R_f = 0.45$) and purified by gel permeation chromatography (GPC). The title compound was obtained as orange solid (53%). $^1\text{H NMR}$ δ 7.62 (s, 1H), 7.50 (d, $J = 7.9$ Hz, 1H), 7.39 (s, $J = 8.2$ Hz, 1H), 4.82 (d, $J = 1.4$ Hz, 1H), 4.59 (t, $J = 2.6$ Hz, 1H), 4.43 (d, $J = 1.4$ Hz, 1H), 3.99 (s, 5H), 0.70 (s, 3H), 0.34 (s, 3H); $^{13}\text{C NMR}$ δ 152.2, 142.9, 128.9 (q, $J_{\text{C-F}} = 4.17, 4.17$ Hz, 1C), 127.0, 126.8, 126.6 (q, $J_{\text{C-F}} = 3.87, 3.58$ Hz, 1C), 121.9, 95.0, 74.0, 72.2, 71.3, 69.9, 64.7, -0.89, -1.77. IR (CH_2Cl_2 cast film): 2929, 2360, 1602, 1323, 1119, 1073; HRMS(ESI) calcd for $\text{C}_{19}\text{H}_{17}\text{F}_3\text{FeSi}$ (M^+): 386.0396; found: 386.0396. $[\alpha]_D^{24} = -245$ (c 0.25, CHCl_3 , 80% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IF-3: 4.6 x 250 mm, 254 nm UV detector, rt, eluent: hexane only, flow rate: 0.5 mL/min, retention time: 11.3 min for major isomer and 12.8 min for minor isomer).

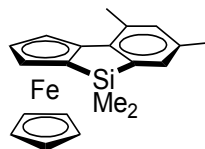




8,8-Dimethyl-6-(trifluoromethoxy)benzosilolo[2,3-a]ferrocene (2fa).

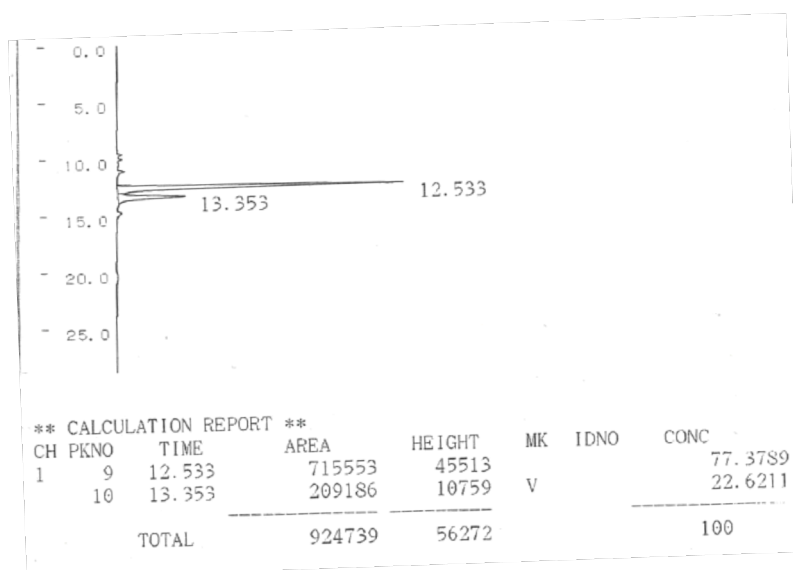
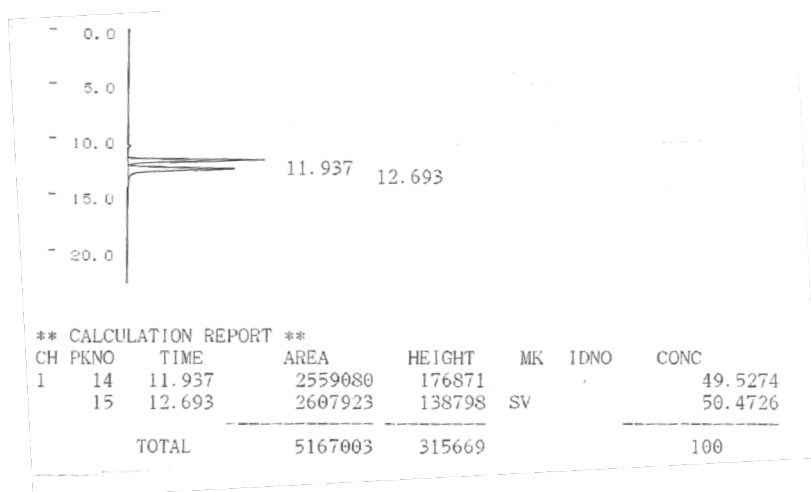
Isolated by thin-layer chromatography (hexane only, $R_f = 0.45$) and purified by gel permeation chromatography (GPC). The title compound was obtained as orange oil (55%). ^1H NMR δ 7.30 (d, $J = 8.2$ Hz, 1H), 7.23 (s, 1H), 7.09 (d, $J = 8.8$ Hz, 1H), 4.75 (d, $J = 1.6$ Hz, 1H), 4.54 (t, $J = 2.2$ Hz, 1H), 4.37 (d, $J = 1.6$ Hz, 1H), 3.99 (s, 5H), 0.68 (s, 3H), 0.32 (s, 3H); ^{13}C NMR δ 147.2, 146.6, 144.5, 124.9, 122.2, 121.5, 119.5, 95.6, 73.5, 71.7, 70.9, 69.8, 64.2, -0.89, -1.71. IR (CH_2Cl_2 cast film): 2926, 2359, 1770, 1255, 1163; HRMS(ESI) calcd for $\text{C}_{19}\text{H}_{17}\text{F}_3\text{FeOSi}$ (M^+): 402.0345; found: 402.0345. $[\alpha]^{24}\text{D} = -175$ (c 0.25, CHCl_3 , 76% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IF-3: 4.6 x 250 mm, 254 nm UV detector, rt, eluent: hexane only, flow rate: 0.5 mL/min, retention time: 11.1 min for major isomer and 12.1 min for minor isomer).

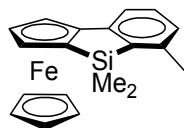




4,6,8,8-Tetramethylbenzosilolo[2,3-a]ferrocene (2ga).

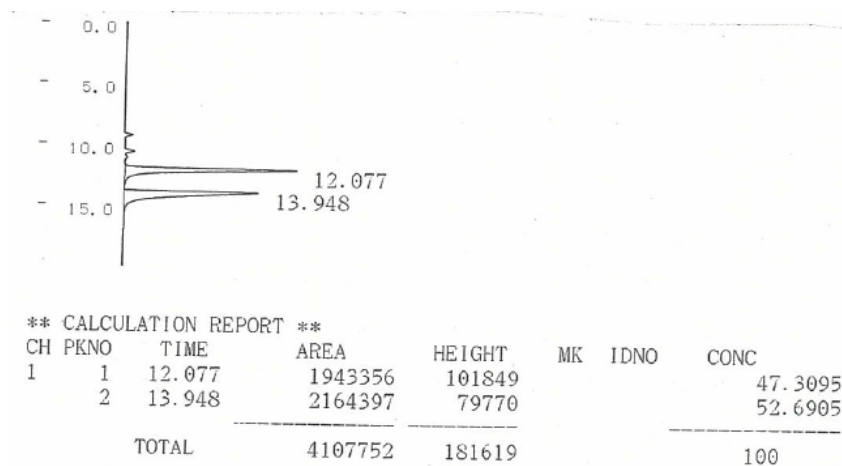
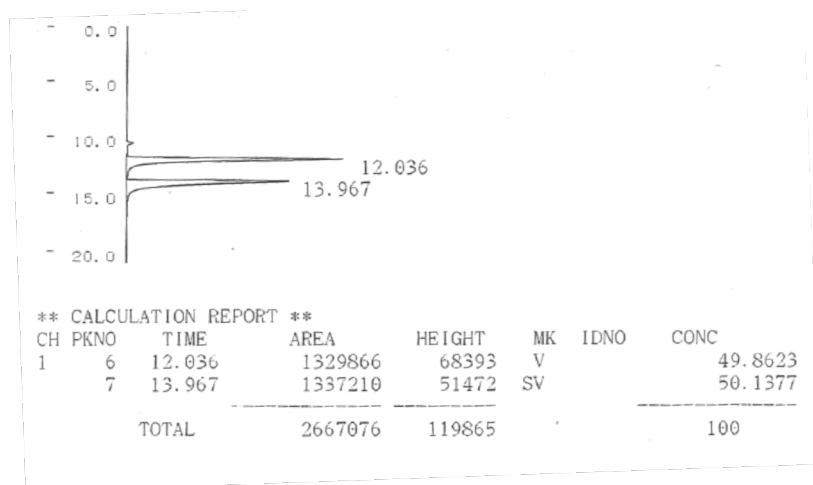
Isolated by thin-layer chromatography (hexane only, $R_f = 0.3$) and purified by gel permeation chromatography (GPC). The title compound was obtained as orange oil (75%). $^1\text{H NMR}$ δ 7.09 (s, 1H), 6.90 (s, 1H), 4.79 (d, $J = 2.1$ Hz, 1H), 4.51 (t, $J = 2.1$ Hz, 1H), 4.33 (d, $J = 2.1$ Hz, 1H), 3.99 (s, 5H), 2.46 (s, 3H), 2.29 (s, 3H), 0.63 (s, 3H), 0.29 (s, 3H); $^{13}\text{C NMR}$ δ 142.0, 141.7, 133.5, 131.6, 130.7, 129.8, 96.2, 72.3, 70.9, 69.2, 68.3, 66.6, 20.1, 20.0, -1.8, -2.6. IR (CH_2Cl_2 cast film): 2921, 2321, 1507, 866, 775 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{20}\text{H}_{22}\text{FeSi}$ (M^+): 346.0835; found: 346.0834. $[\alpha]_D^{19} = -71$ (c 0.68, CHCl_3 , 55% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IF-3: 4.6 x 250 mm, 254 nm UV detector, rt, eluent: hexane only, flow rate: 0.5 mL/min, retention time: 12.2 min for major isomer and 13.0 min for minor isomer).

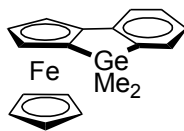




7,8,8-Trimethyl-benzosilolo[2,3-a]ferrocene (2ha).

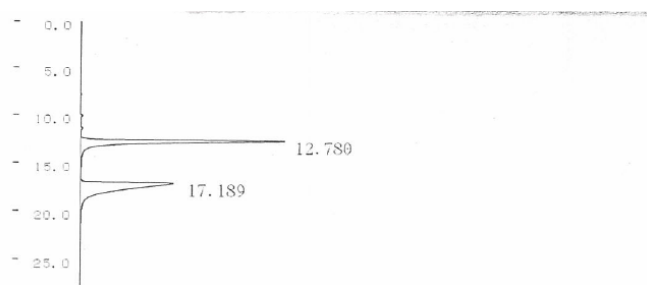
Isolated by thin-layer chromatography (hexane only, $R_f = 0.3$) and purified by gel permeation chromatography (GPC). The title compound was obtained as orange oil (67%). ^1H NMR δ 7.17 (d, $J = 4.4$ Hz, 2H), 6.92 (t, $J = 4.4$ Hz, 1H), 4.75 (d, $J = 2.2$ Hz, 1H), 4.50 (t, $J = 2.2$ Hz, 1H), 4.34 (d, $J = 2.2$ Hz, 1H), 3.98 (s, 5H), 2.39 (s, 3H), 0.72 (s, 3H), 0.36 (s, 3H); ^{13}C NMR δ 149.1, 146.8, 132.6, 126.3, 121.7, 116.9, 95.4, 73.9, 71.8, 71.0, 69.8, 69.6, 64.5, -0.9, -1.8. IR (CH_2Cl_2 cast film): 2922, 2359, 1245, 785, 439 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{19}\text{H}_{20}\text{FeSi}$ (M^+): 332.0678; found: 332.0678. $[\alpha]_{\text{D}}^{18} = -13$ (c 0.55, CHCl_3 , 5% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA-3: 4.6 x 250 mm, 254 nm UV detector, rt, eluent: hexane only, flow rate: 0.5 mL/min, retention time: 13.9 min for major isomer and 12.0 min for minor isomer).





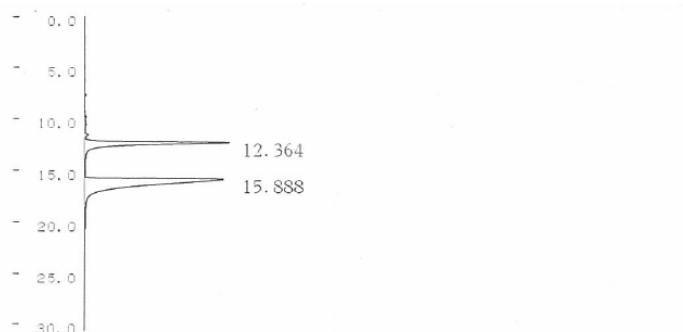
8,8-Dimethylbenzogermylo[2,3-a]ferrocene (5).

Isolated by thin-layer chromatography (hexane only, $R_f = 0.3$). The title compound was obtained as orange oil (40%). $^1\text{H NMR}$ δ 7.43 (d, $J = 7.1$ Hz, 1H), 7.38 (d, $J = 7.4$ Hz, 1H), 7.22-7.28 (m, 1H, overlap with CHCl_3), 7.13 (t, $J = 7.4$ Hz, 1H), 4.76 (s, 1H), 4.48 (s, 1H), 4.37 (s, 1H), 3.97 (s, 5H), 0.83 (s, 3H), 0.49 (s, 3H); $^{13}\text{C NMR}$ δ 146.6, 144.4, 132.6, 128.9, 125.4, 121.4, 95.7, 75.4, 72.4, 70.5, 69.5, 63.7, -0.6, -1.0. IR (CH_2Cl_2 cast film): 2960, 1727, 1268, 1124, 767 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{FeGe}$ (M^+): 359.9995; found: 359.9996. $[\alpha]_D^{15} = -184$ (c 0.19, CHCl_3 , 33% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA-3: 4.6 x 250 mm, 254 nm UV detector, rt, eluent: hexane only, flow rate: 0.5 mL/min, retention time: 15.9 min for major isomer and 12.4 min for minor isomer).



** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
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	28	17.189	1789119	35128	SV		49.8758
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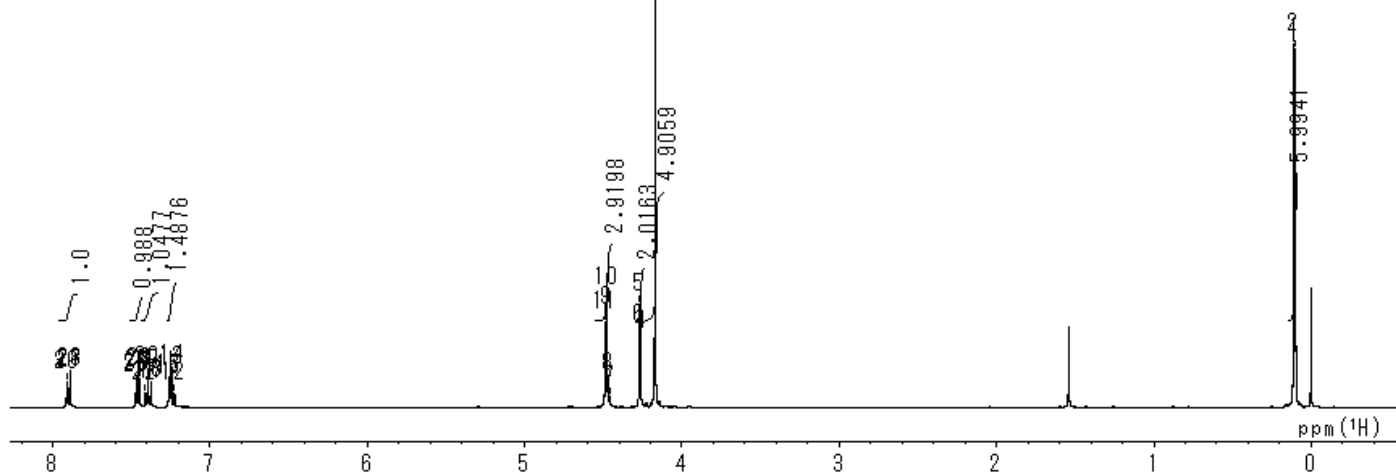
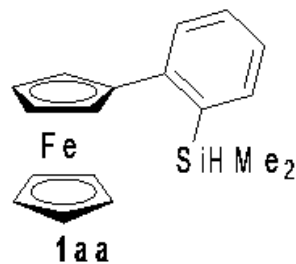


** CALCULATION REPORT **

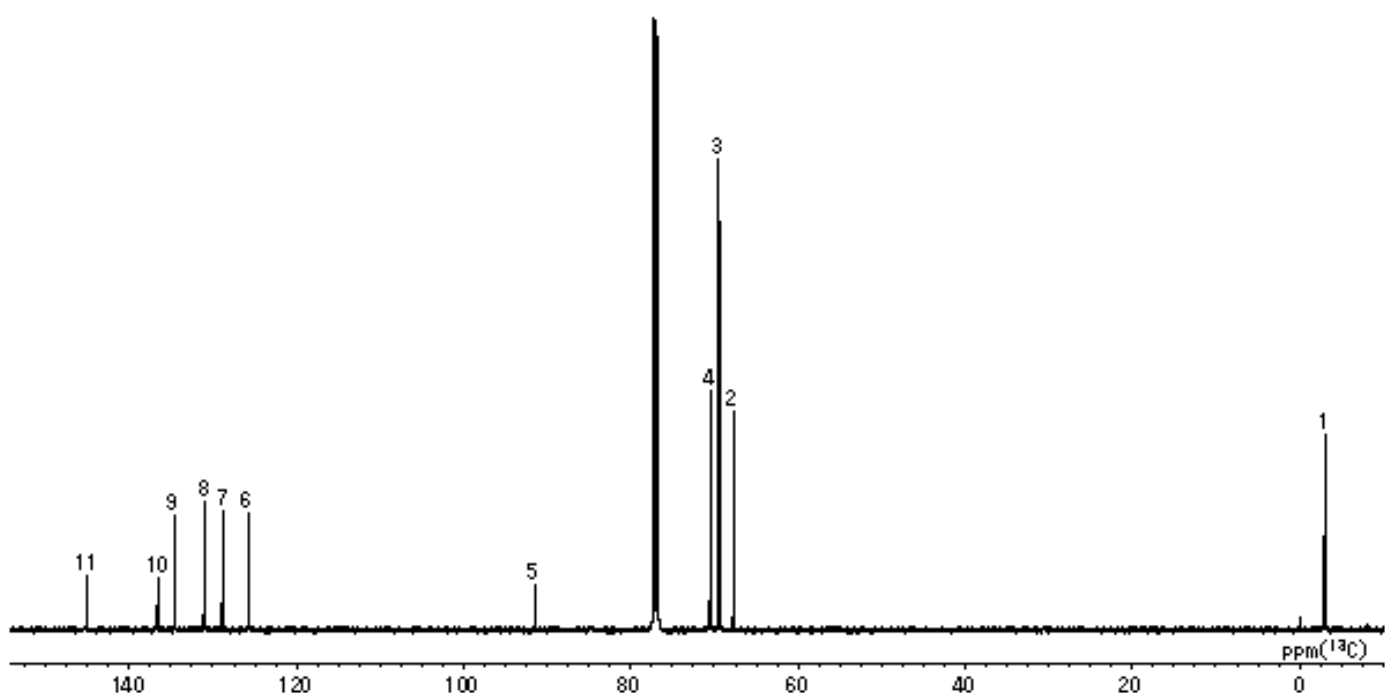
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	20	12.364	1089891	51485	SV		33.5081
	23	15.888	2162732	49636	SV		66.4919
TOTAL			3252623	101121			100

No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height
1	0.10	63.81	8	4.47	4.38	15	7.26	4.01	22	7.41	2.72	29	7.91	4.67
2	0.11	64.70	9	4.48	16.20	16	7.26	3.73	23	7.45	5.10	30	7.91	4.61
3	4.17	99.97	10	4.48	19.62	17	7.37	2.91	24	7.45	4.78			
4	4.26	11.76	11	4.49	15.27	18	7.38	3.29	25	7.47	4.28			
5	4.27	18.44	12	7.23	2.56	19	7.39	4.85	26	7.47	3.98			
6	4.27	13.05	13	7.24	5.59	20	7.40	5.32	27	7.89	5.00			
7	4.46	1.94	14	7.24	5.80	21	7.41	2.61	28	7.89	5.04			

No.	Start (ppm)	End (ppm)	Integral
1	0.1452	0.0863	5.9941
2	4.2295	4.1098	4.9059
3	4.2973	4.2295	2.0163
4	4.5485	4.4371	2.9198
5	7.2749	7.2133	1.4876
6	7.4314	7.3244	1.0477
7	7.5074	7.4314	0.988
8	7.9562	7.8336	1.0

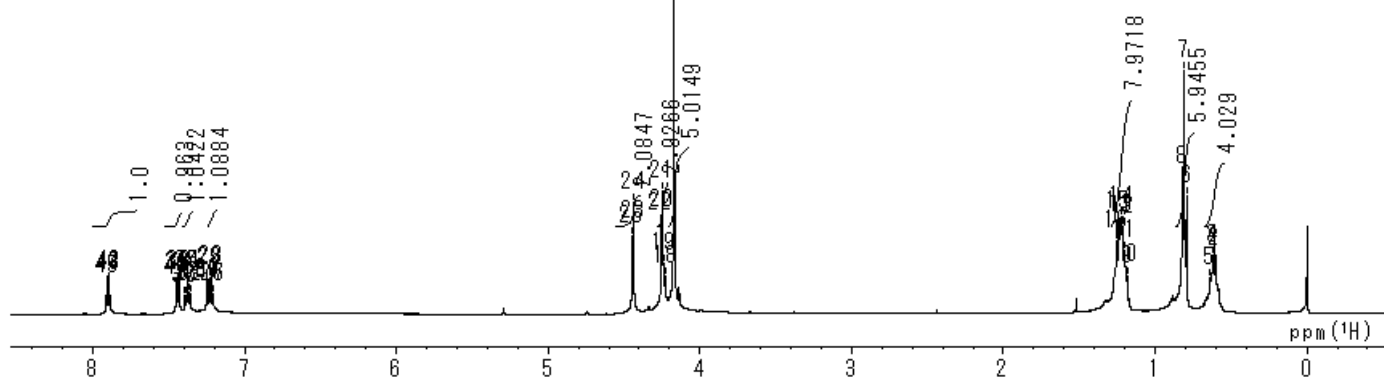
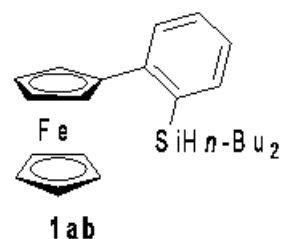


No.	δ /ppm	Height	No.	δ /ppm	Height
1	-3.01	30.78	7	128.87	18.09
2	67.72	34.26	8	131.07	19.51
3	69.45	75.51	9	134.61	17.45
4	70.52	37.63	10	136.62	7.10
5	91.44	6.09	11	145.04	7.61
6	125.71	17.69			

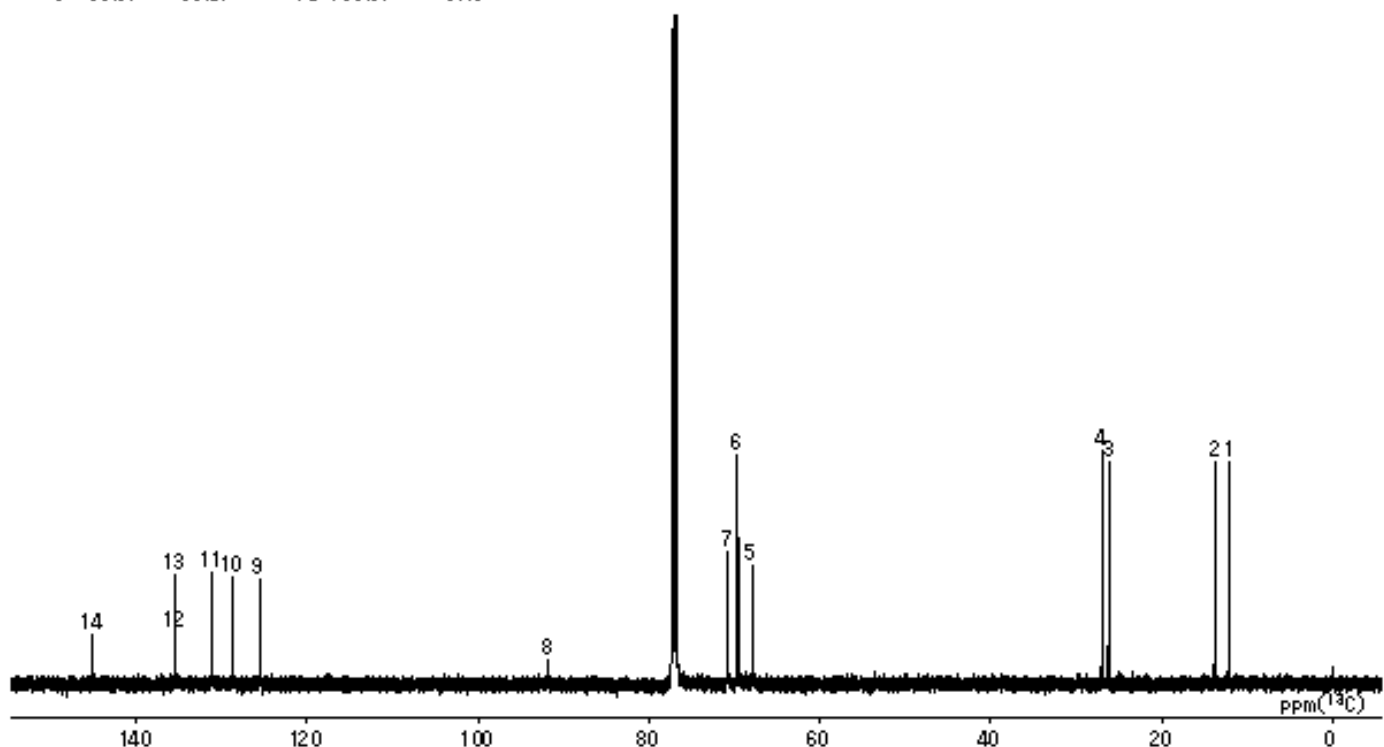


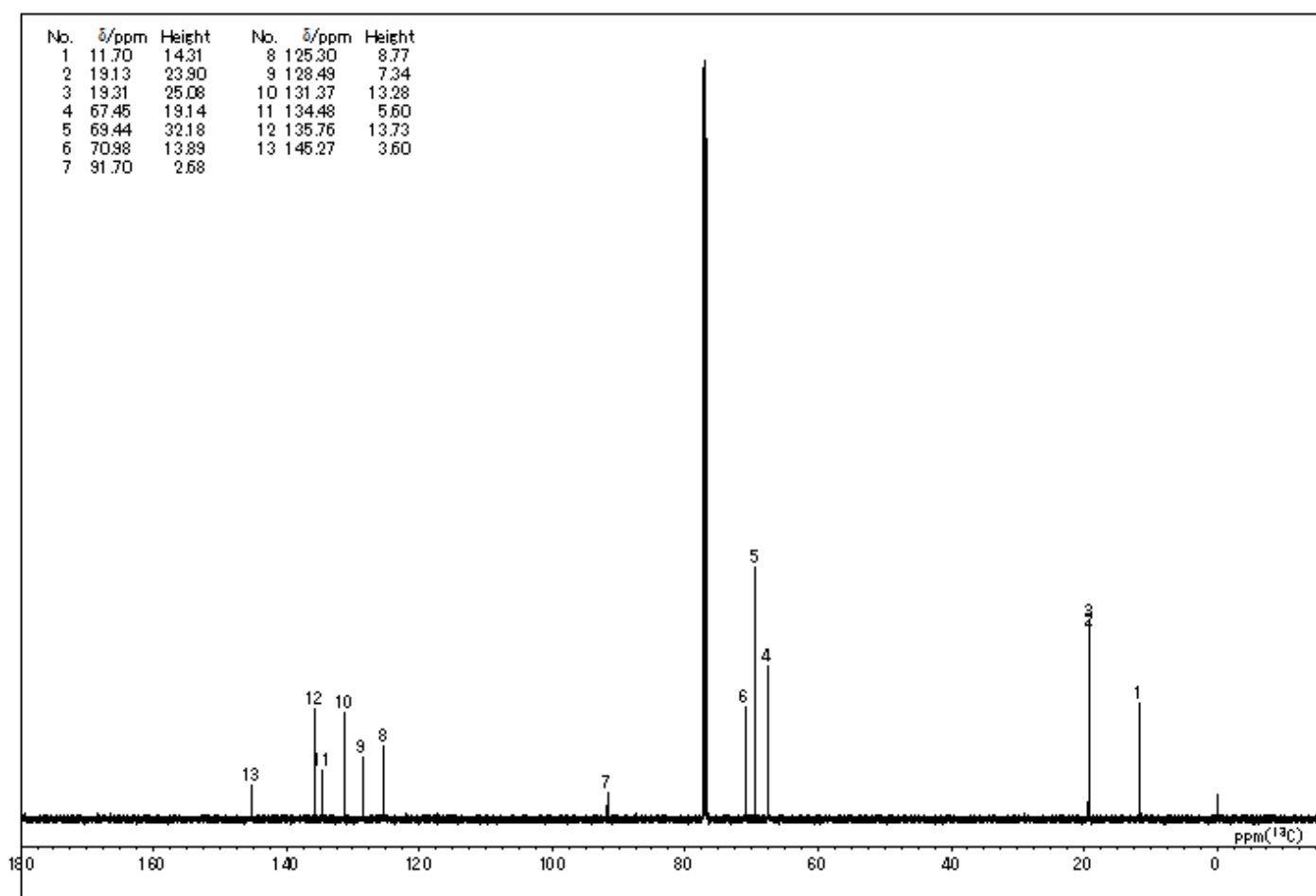
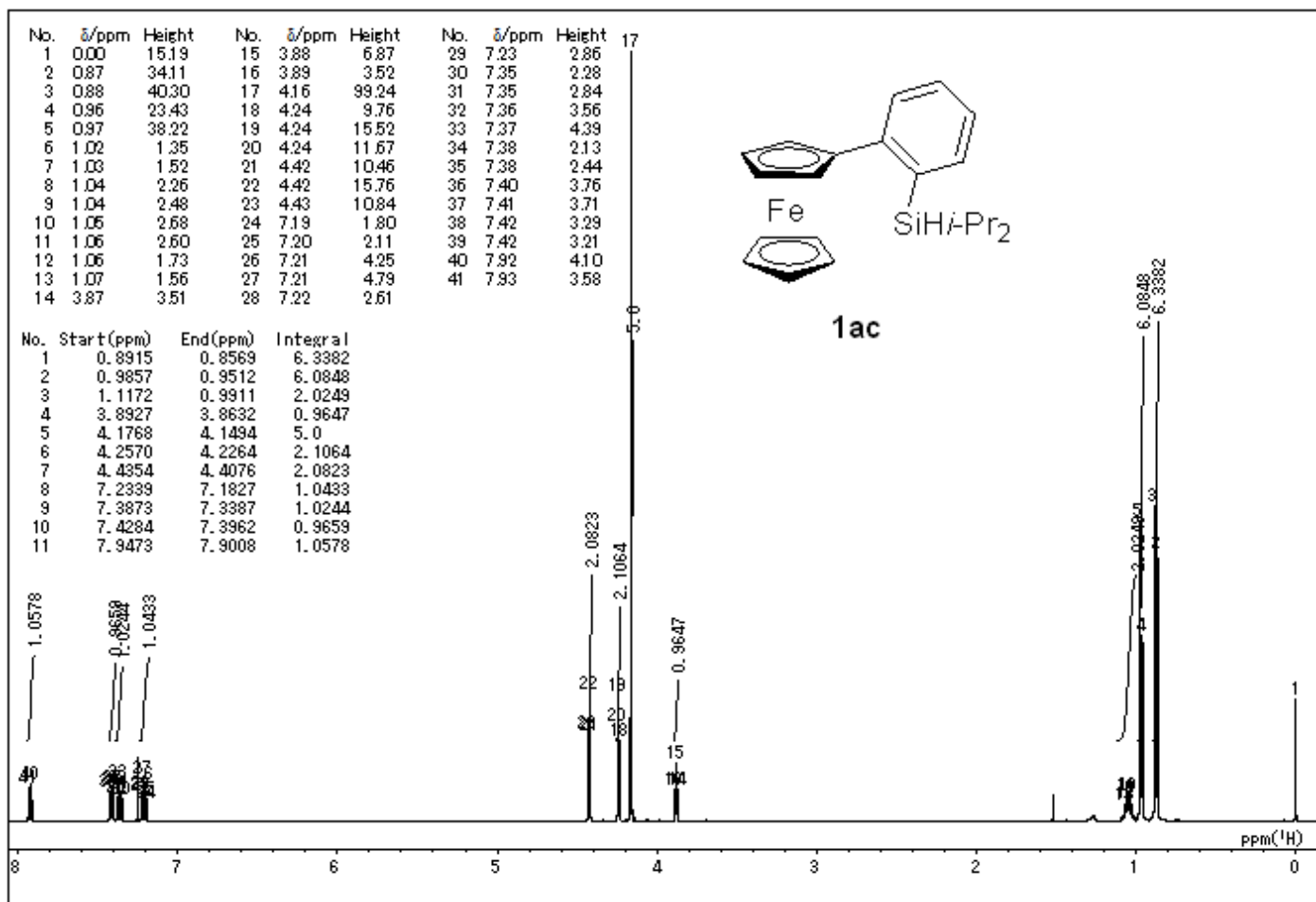
No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height
1	0.60	8.97	10	1.19	6.89	19	4.24	8.96	28	7.22	6.47	37	7.39	3.03
2	0.61	9.70	11	1.20	11.16	20	4.24	16.63	29	7.22	6.24	38	7.43	5.63
3	0.62	10.47	12	1.21	15.44	21	4.25	21.90	30	7.24	4.29	39	7.44	5.46
4	0.62	10.24	13	1.22	15.74	22	4.25	16.15	31	7.24	4.10	40	7.45	4.84
5	0.64	6.34	14	1.23	17.14	23	4.44	14.59	32	7.36	3.59	41	7.45	4.52
6	0.79	20.94	15	1.24	16.48	24	4.44	19.82	33	7.36	3.72	42	7.89	5.63
7	0.81	43.35	16	1.25	12.93	25	4.44	13.88	34	7.37	5.65	43	7.89	5.53
8	0.82	24.36	17	4.17	99.95	26	7.21	3.39	35	7.38	5.61	44	7.91	5.18
9	1.18	6.53	18	4.23	6.47	27	7.21	3.43	36	7.39	3.24	45	7.91	4.89

No.	Start (ppm)	End (ppm)	Integral
1	0.6683	0.5391	4.029
2	0.8597	0.7355	5.9455
3	1.2885	1.1481	7.9718
4	4.2061	4.0640	5.0149
5	4.2741	4.2061	2.9266
6	4.5543	4.3783	2.0847
7	7.2427	7.1738	1.0884
8	7.4095	7.3370	1.0422
9	7.5234	7.4095	0.963
10	8.0008	7.7042	1.0



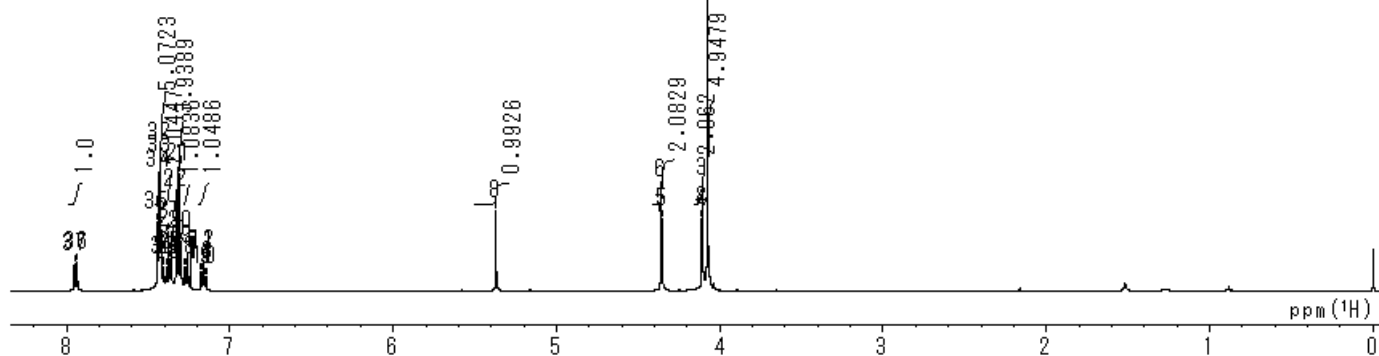
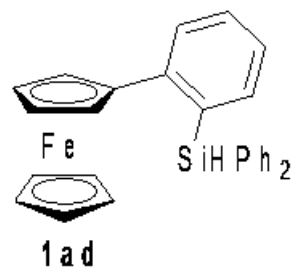
No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height
1	12.13	32.04	7	70.75	18.41	13	135.45	15.13
2	13.73	31.99	8	91.89	2.50	14	145.09	6.12
3	26.18	32.03	9	125.59	14.45			
4	26.95	33.55	10	128.67	14.87			
5	67.78	16.48	11	131.21	15.29			
6	69.61	33.07	12	135.37	6.45			



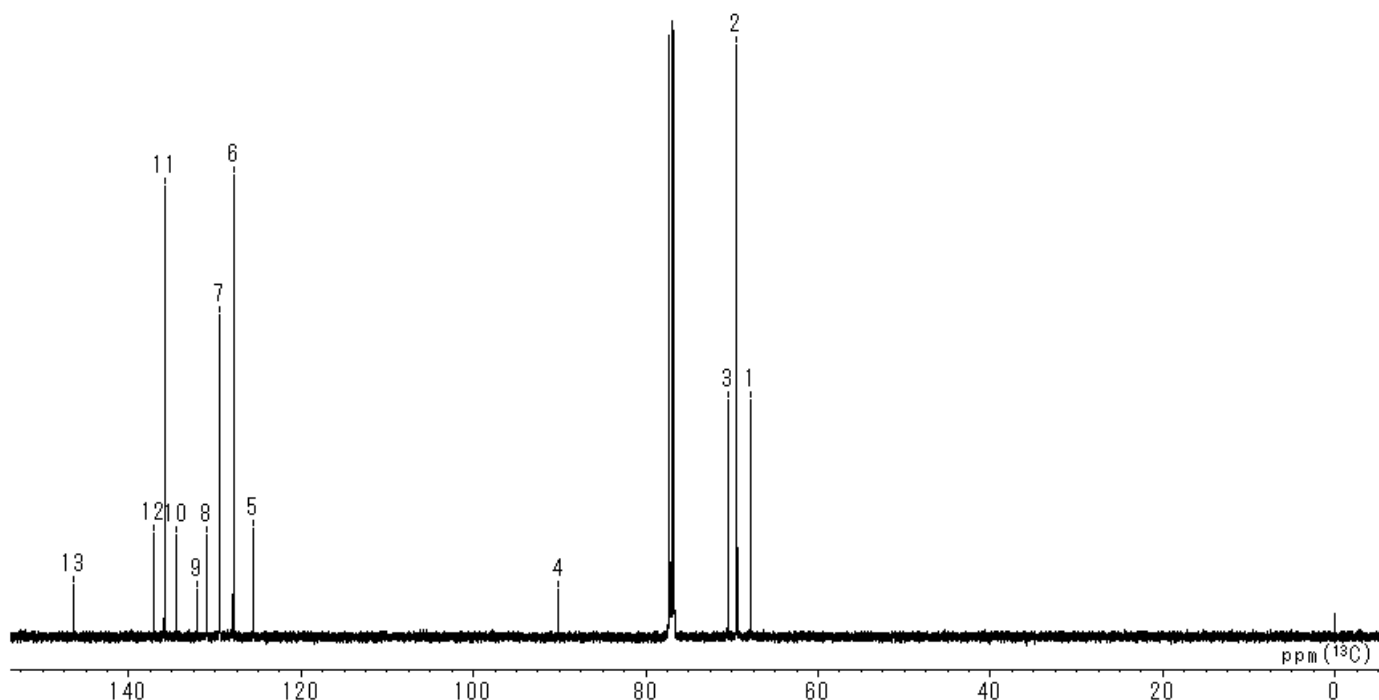


No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height
1	4.08	100.00	8	5.37	13.08	15	7.26	4.79	22	7.33	14.86	29	7.39	3.80	36	7.94	4.64
2	4.10	11.97	9	7.15	2.27	16	7.26	5.03	23	7.36	4.82	30	7.40	3.87	37	7.95	4.33
3	4.11	16.78	10	7.15	2.31	17	7.27	3.99	24	7.36	8.43	31	7.41	3.95			
4	4.11	11.72	11	7.16	4.95	18	7.28	3.89	25	7.36	5.86	32	7.42	22.59			
5	4.35	11.81	12	7.16	4.89	19	7.30	5.80	26	7.37	3.89	33	7.43	20.41			
6	4.36	16.49	13	7.18	3.23	20	7.30	8.11	27	7.37	9.75	34	7.44	17.95			
7	4.36	10.63	14	7.18	3.07	21	7.31	19.03	28	7.38	3.19	35	7.44	11.26			

No.	Start (ppm)	End (ppm)	Integral
1	4.0962	4.0291	4.9479
2	4.1502	4.0962	2.062
3	4.4083	4.2694	2.0829
4	5.4977	5.2834	0.9926
5	7.1889	7.1213	1.0486
6	7.2834	7.2488	1.0836
7	7.3397	7.2877	3.9389
8	7.3933	7.3531	2.0447
9	7.4580	7.3933	5.0723
10	7.9831	7.9019	1.0

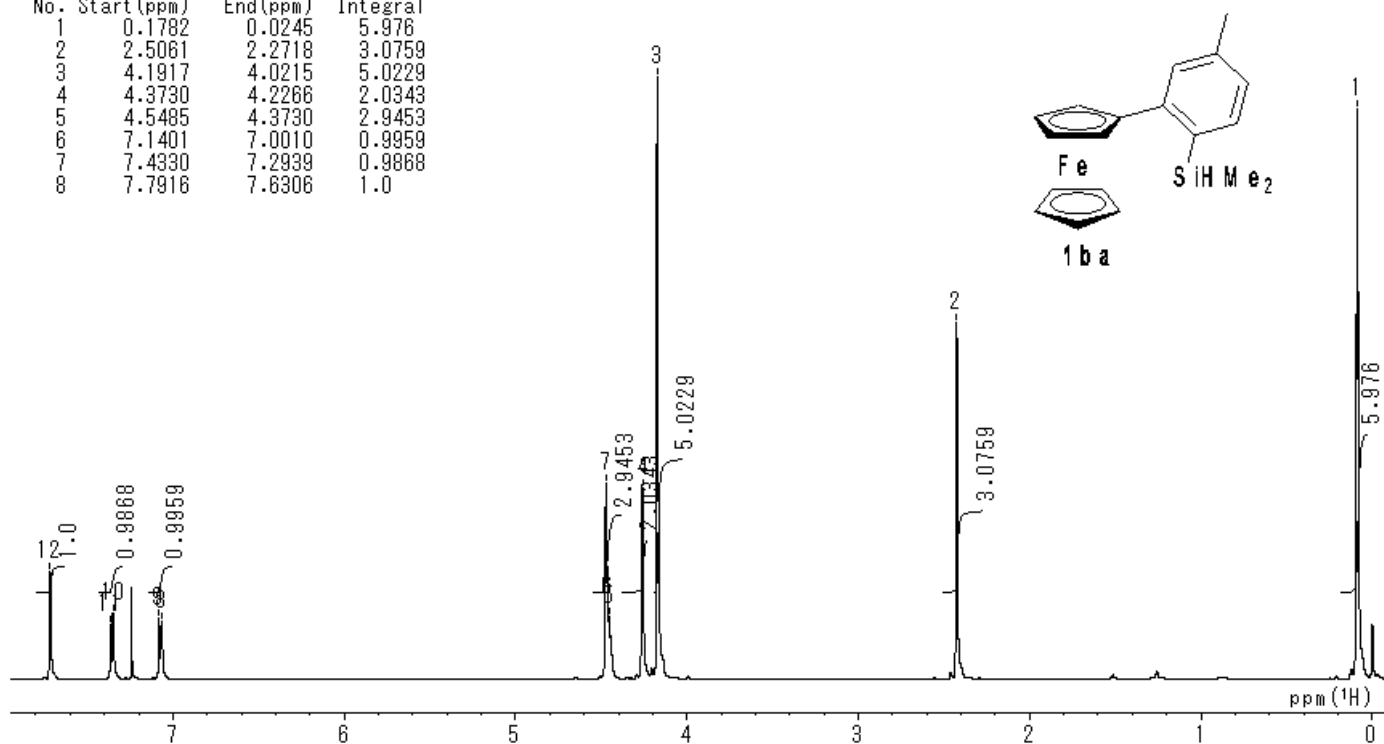


No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height
1	67.81	38.30	6	127.85	74.92	11	135.84	73.23
2	69.43	96.20	7	129.44	52.33	12	137.04	16.86
3	70.49	38.33	8	130.93	16.58	13	146.33	8.35
4	90.17	7.56	9	132.03	7.47			
5	125.52	17.47	10	134.50	16.44			

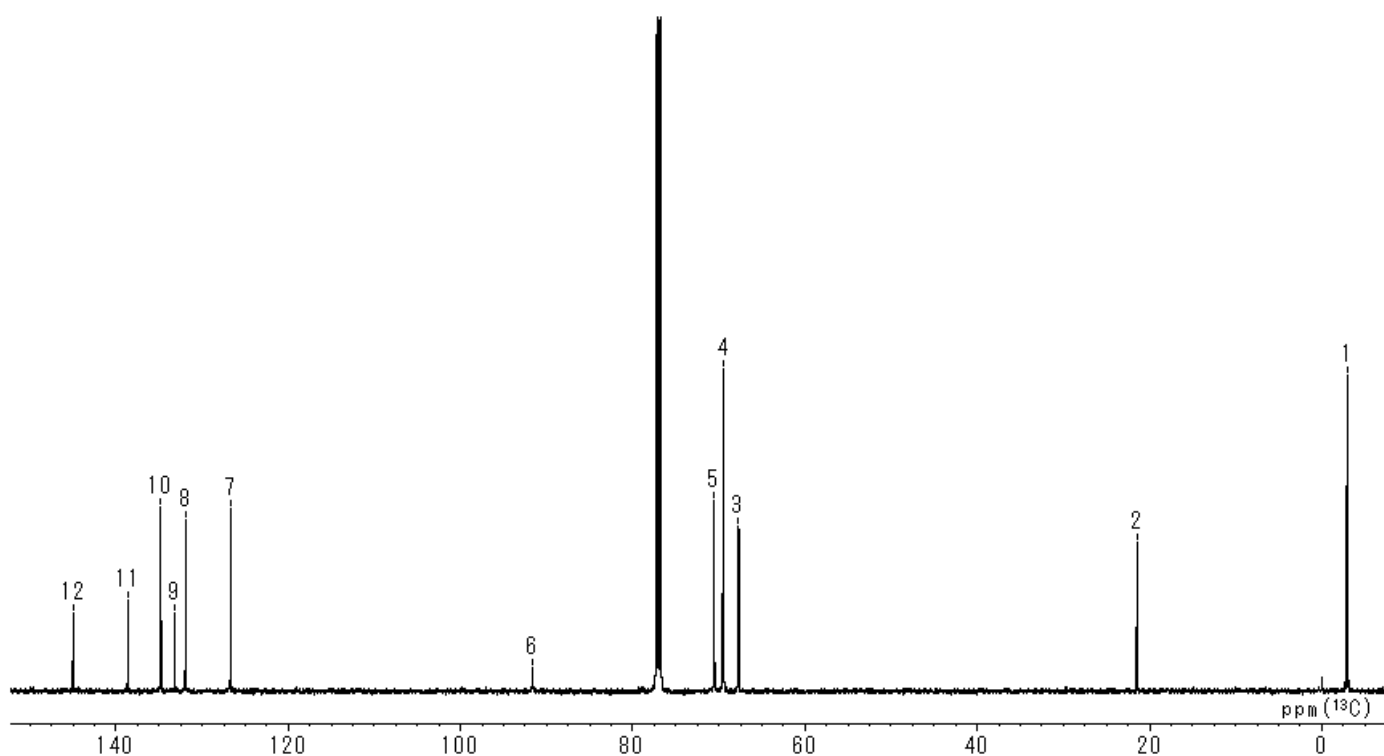


No.	δ /ppm	Height	No.	δ /ppm	Height
1	0.09	84.43	8	7.07	8.67
2	2.43	52.86	9	7.08	8.94
3	4.17	89.08	10	7.35	9.80
4	4.26	28.35	11	7.37	8.06
5	4.45	9.26	12	7.72	16.00
6	4.46	10.73			
7	4.47	29.06			

No.	Start (ppm)	End (ppm)	Integral
1	0.1782	0.0245	5.976
2	2.5061	2.2718	3.0759
3	4.1917	4.0215	5.0229
4	4.3730	4.2266	2.0343
5	4.5485	4.3730	2.9453
6	7.1401	7.0010	0.9959
7	7.4330	7.2939	0.9868
8	7.7916	7.6306	1.0

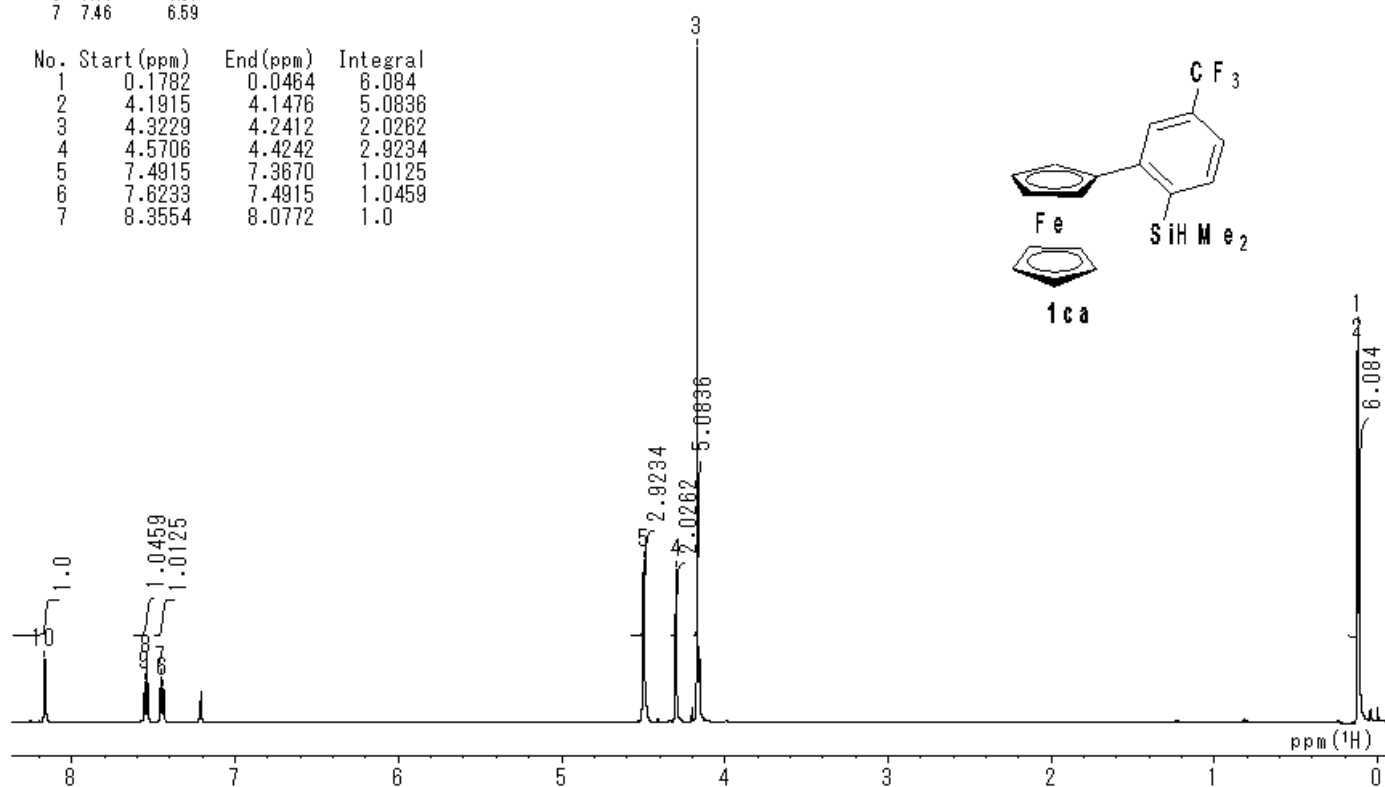
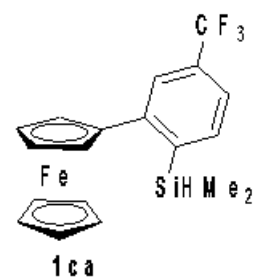


No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height
1	-293	46.62	6	91.60	3.38	11	138.64	13.36
2	21.48	21.92	7	126.70	26.75	12	145.01	11.33
3	67.70	24.16	8	131.94	25.17			
4	69.50	47.43	9	133.14	11.37			
5	70.53	27.98	10	134.79	27.17			

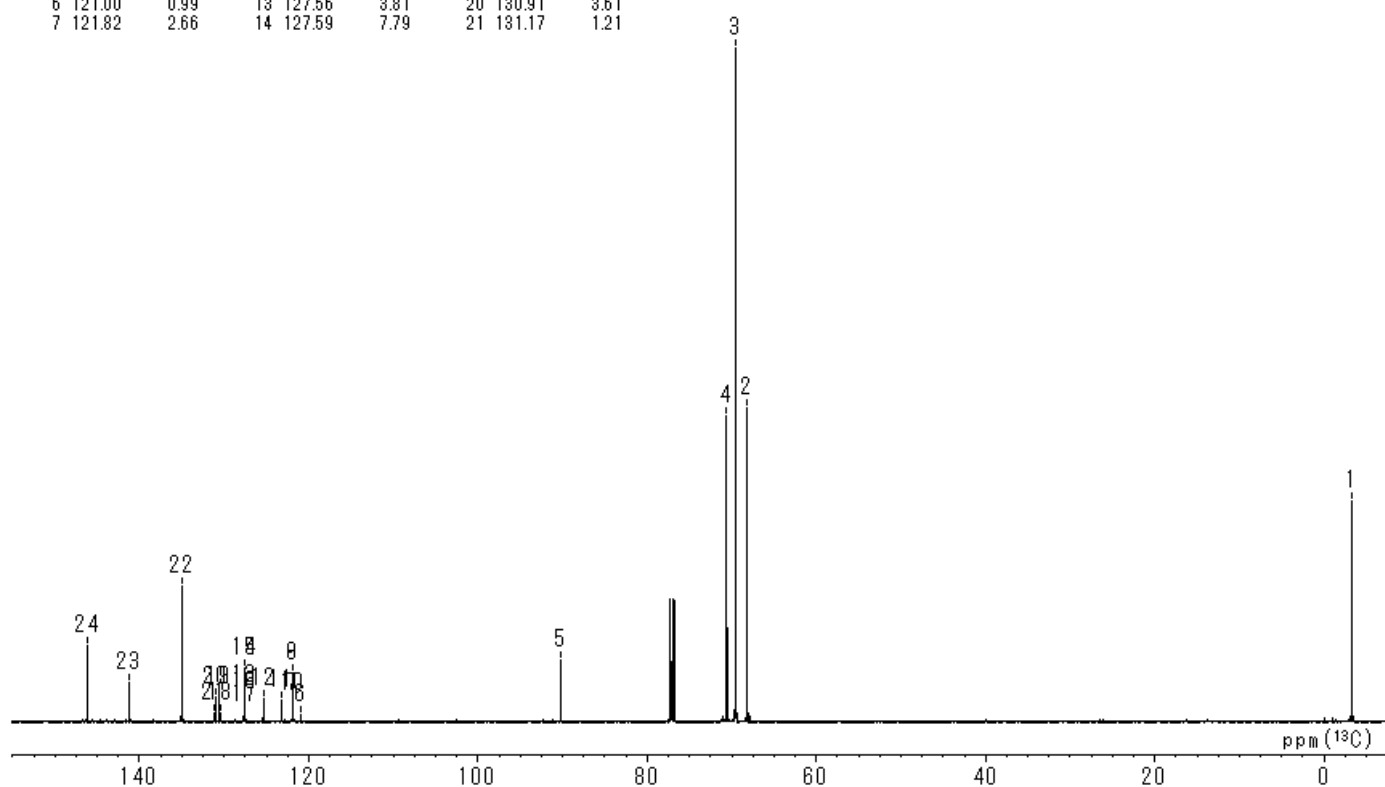


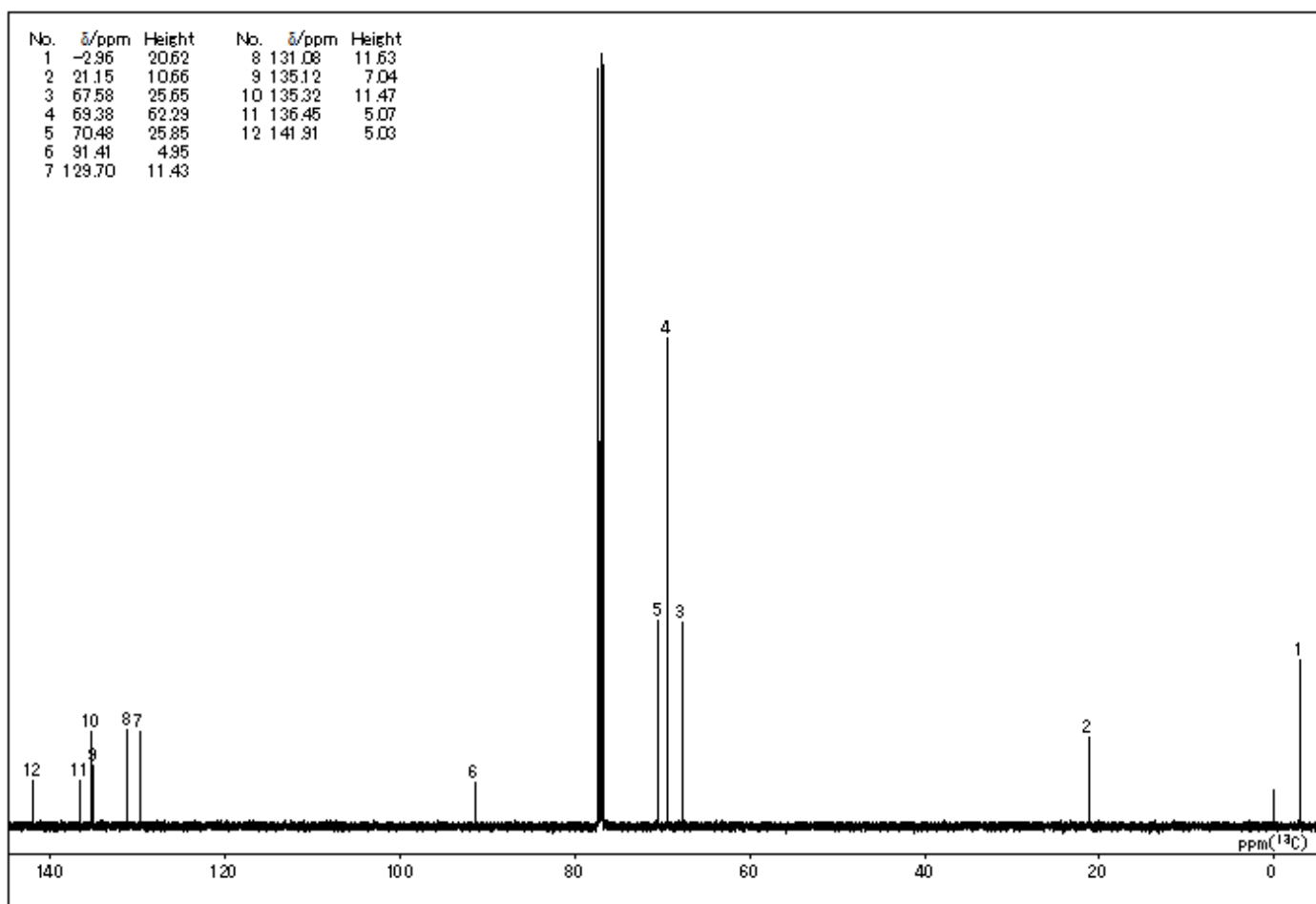
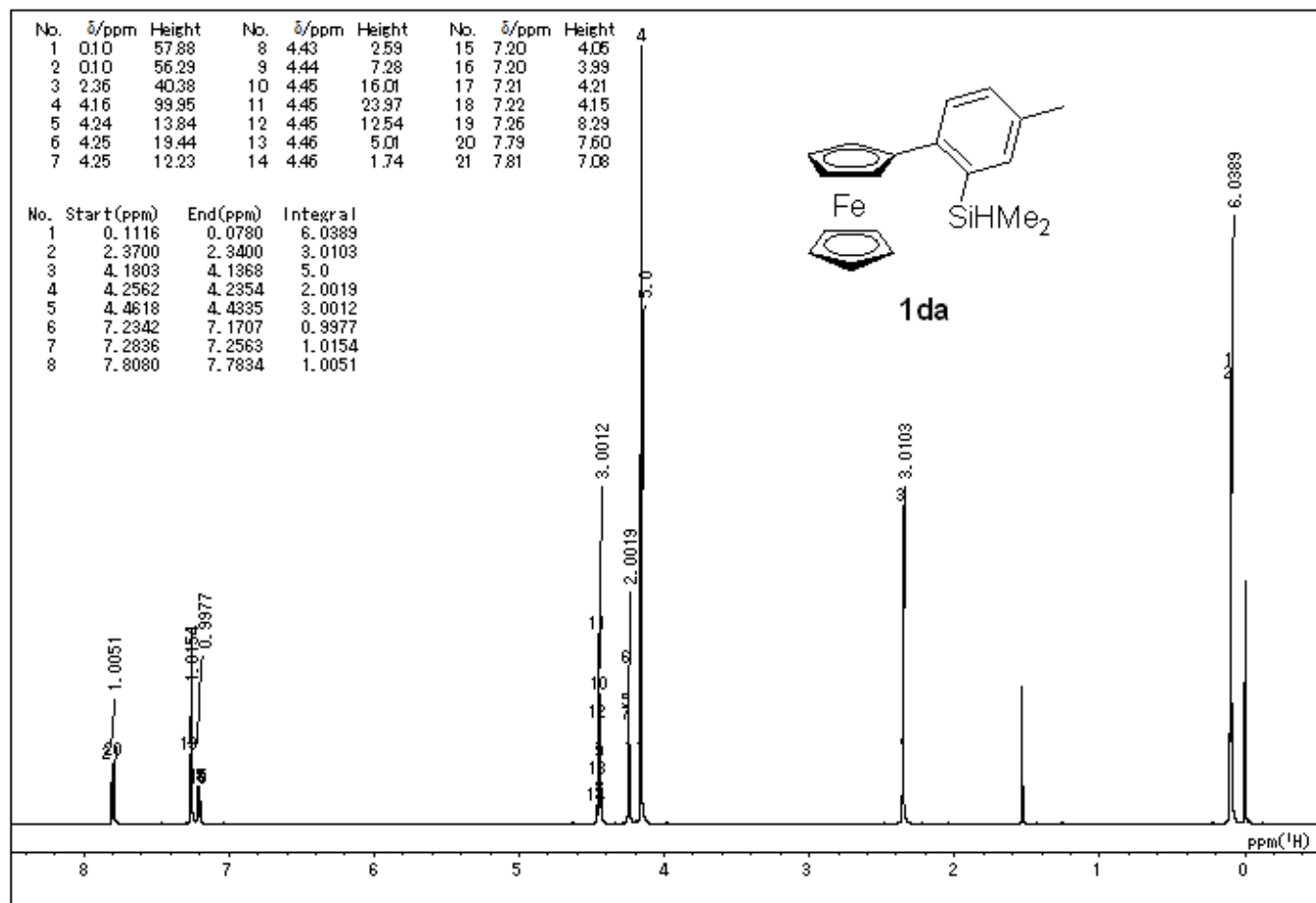
No.	δ /ppm	Height	No.	δ /ppm	Height
1	0.12	58.60	8	7.54	8.21
2	0.12	55.14	9	7.55	5.99
3	4.17	99.75	10	8.17	9.38
4	4.30	22.46			
5	4.50	24.08			
6	7.44	4.97			
7	7.46	6.59			

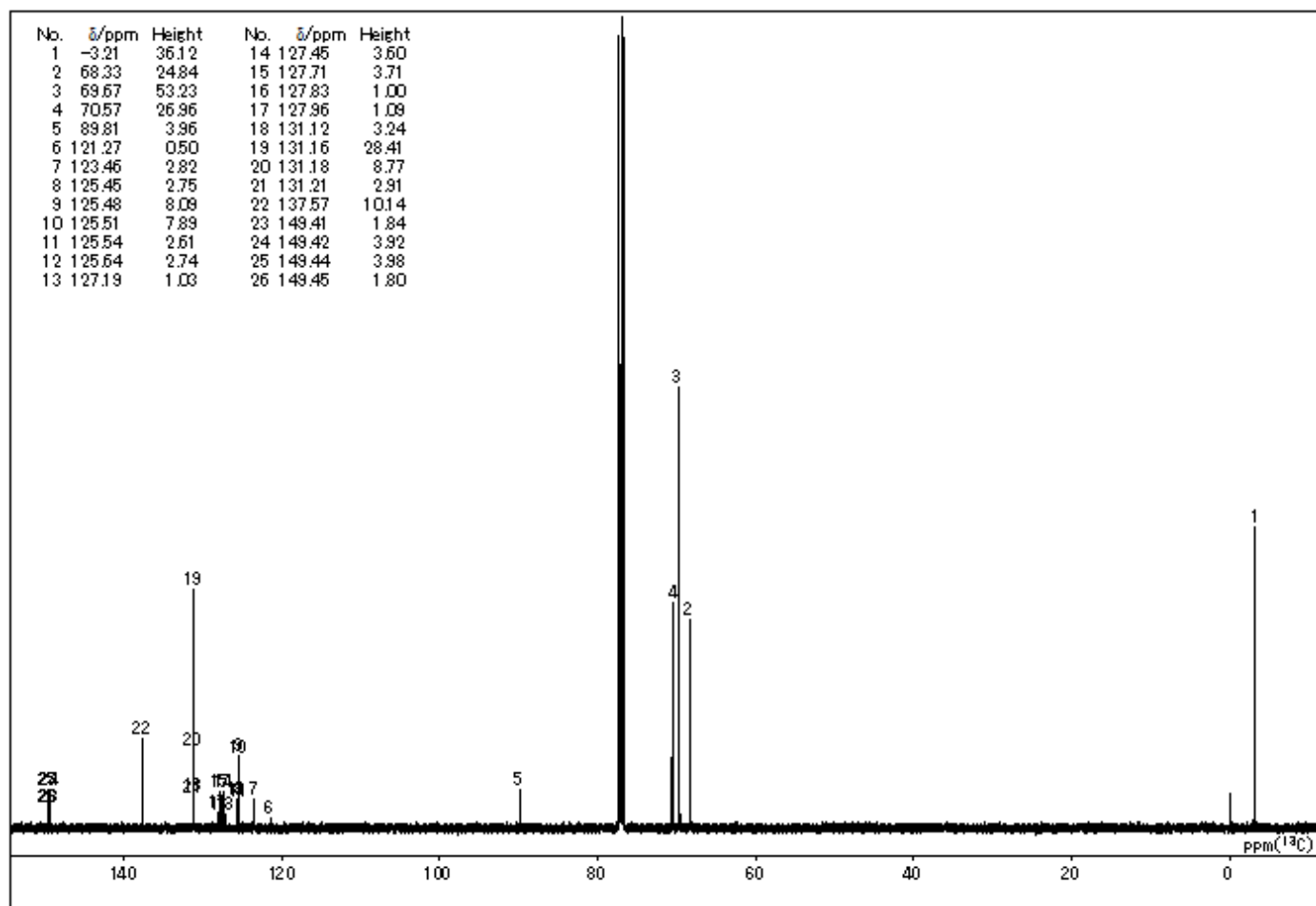
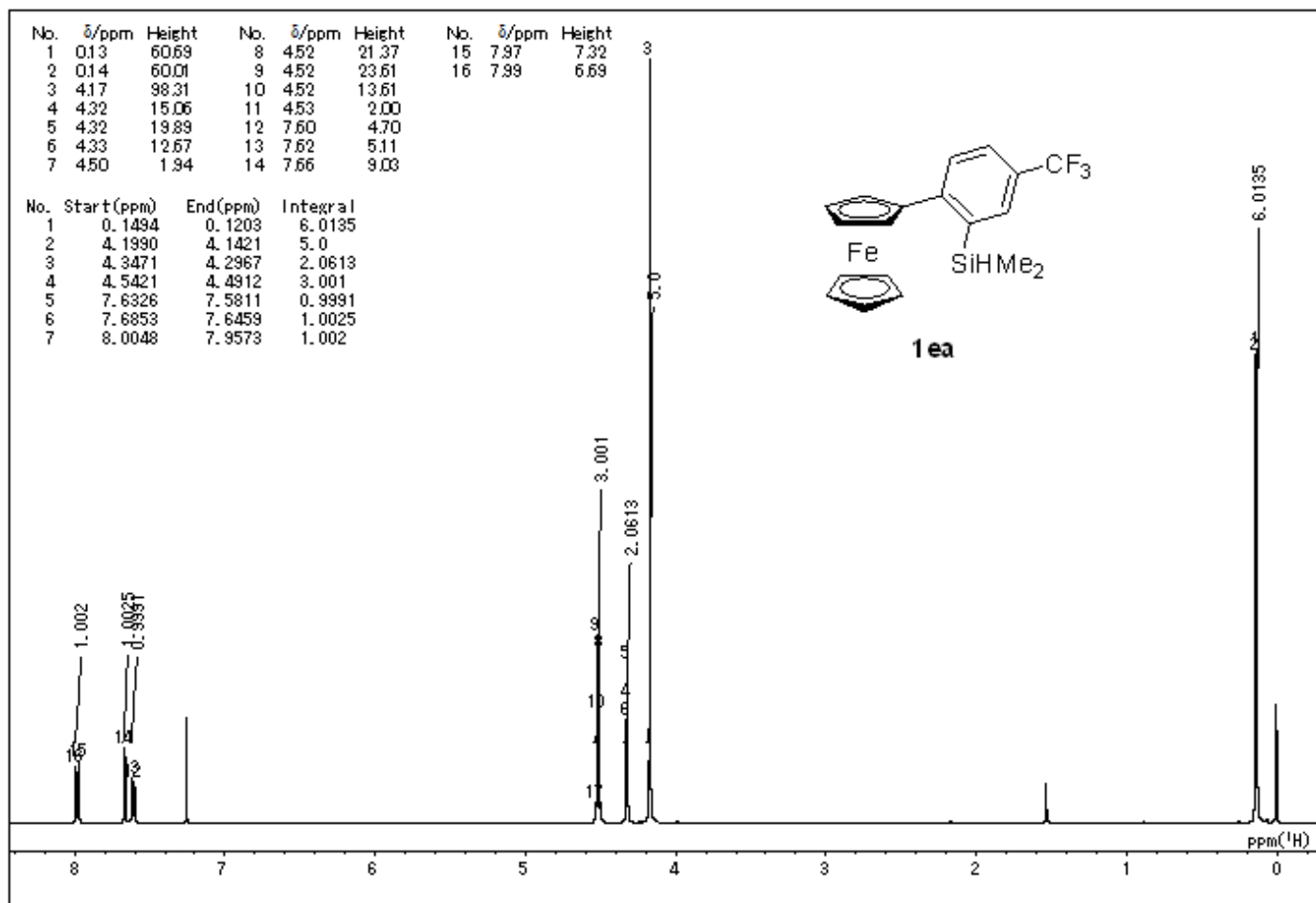
No.	Start (ppm)	End (ppm)	Integral
1	0.1782	0.0464	6.084
2	4.1915	4.1476	5.0836
3	4.3229	4.2412	2.0262
4	4.5706	4.4242	2.9234
5	7.4915	7.3670	1.0125
6	7.6233	7.4915	1.0459
7	8.3554	8.0772	1.0

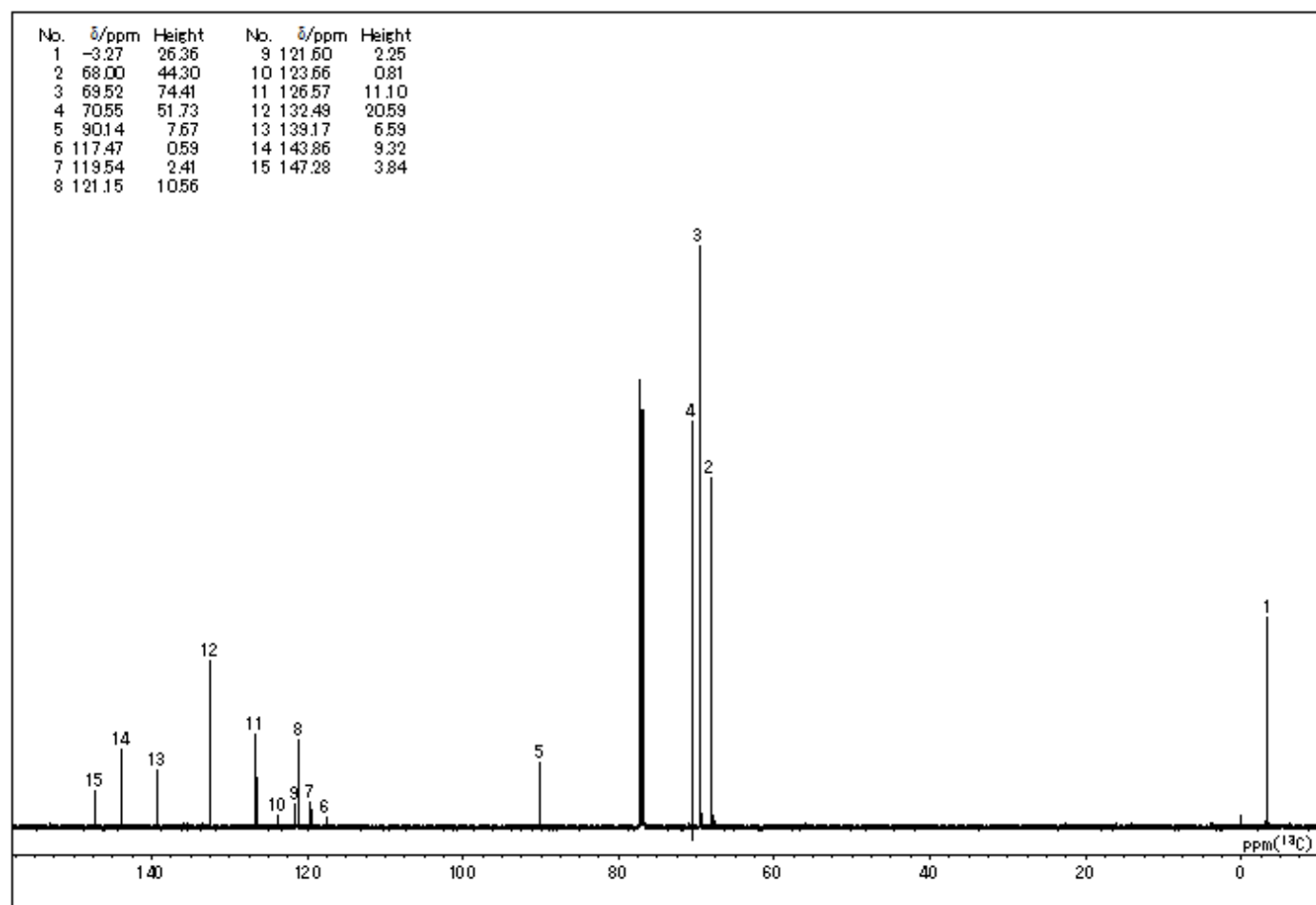
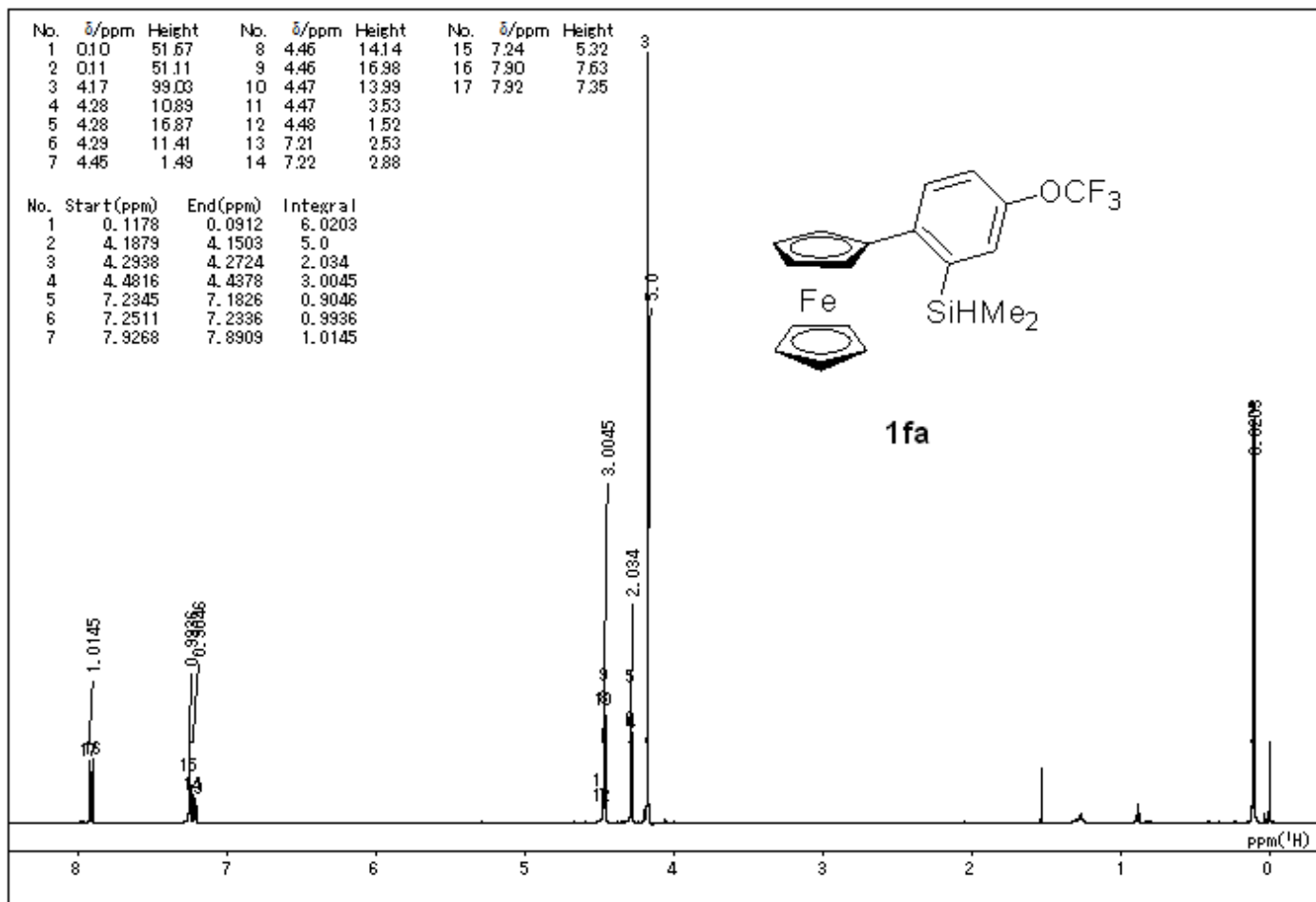


No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height
1	-3.26	32.46	8	121.85	7.04	15	127.62	7.81	22	135.02	20.04
2	68.16	46.41	9	121.88	7.05	16	127.65	2.81	23	141.25	5.71
3	69.58	99.55	10	121.90	2.64	17	127.66	0.92	24	146.22	11.23
4	70.59	45.04	11	123.18	3.01	18	130.40	1.20			
5	90.20	9.04	12	125.37	3.30	19	130.66	3.62			
6	121.00	0.99	13	127.56	3.81	20	130.91	3.61			
7	121.82	2.66	14	127.59	7.79	21	131.17	1.21			



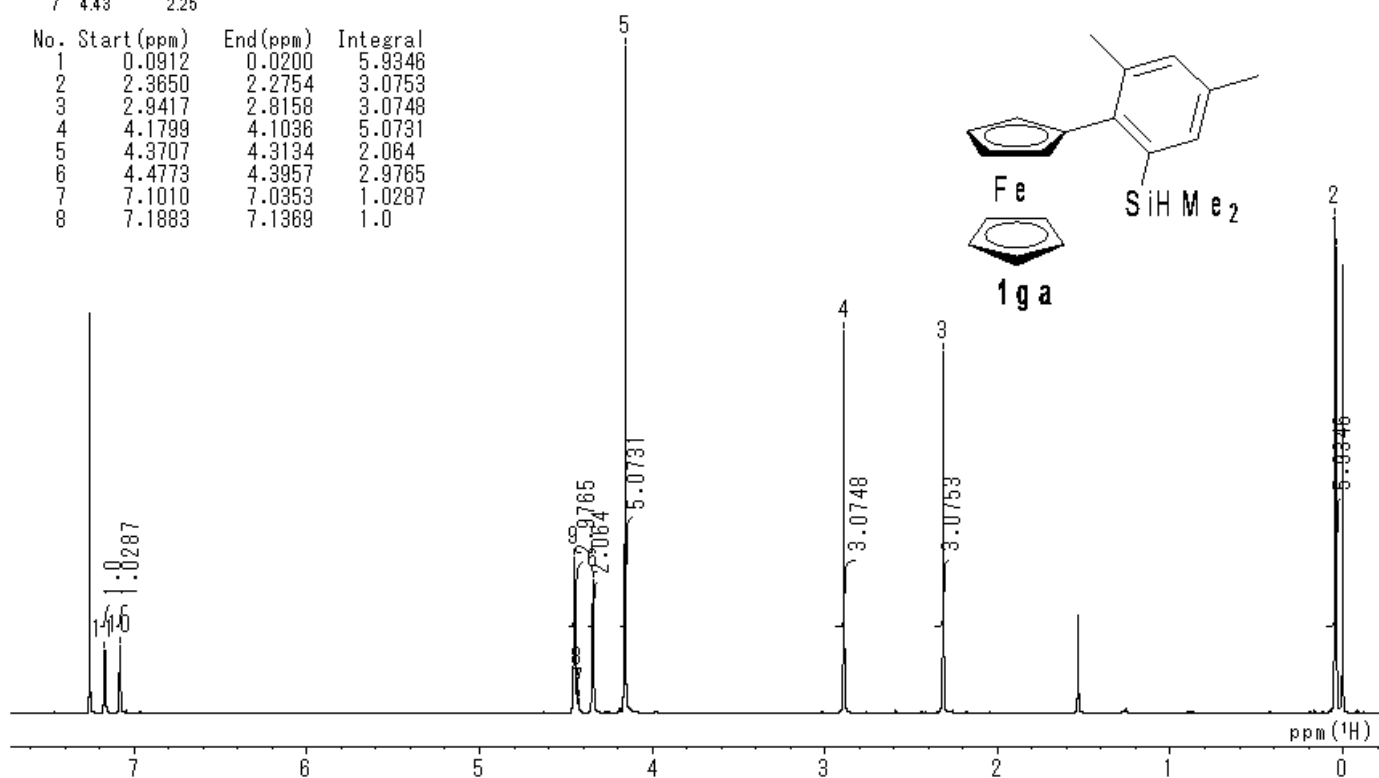
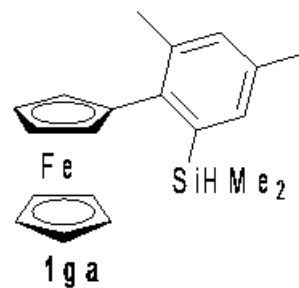




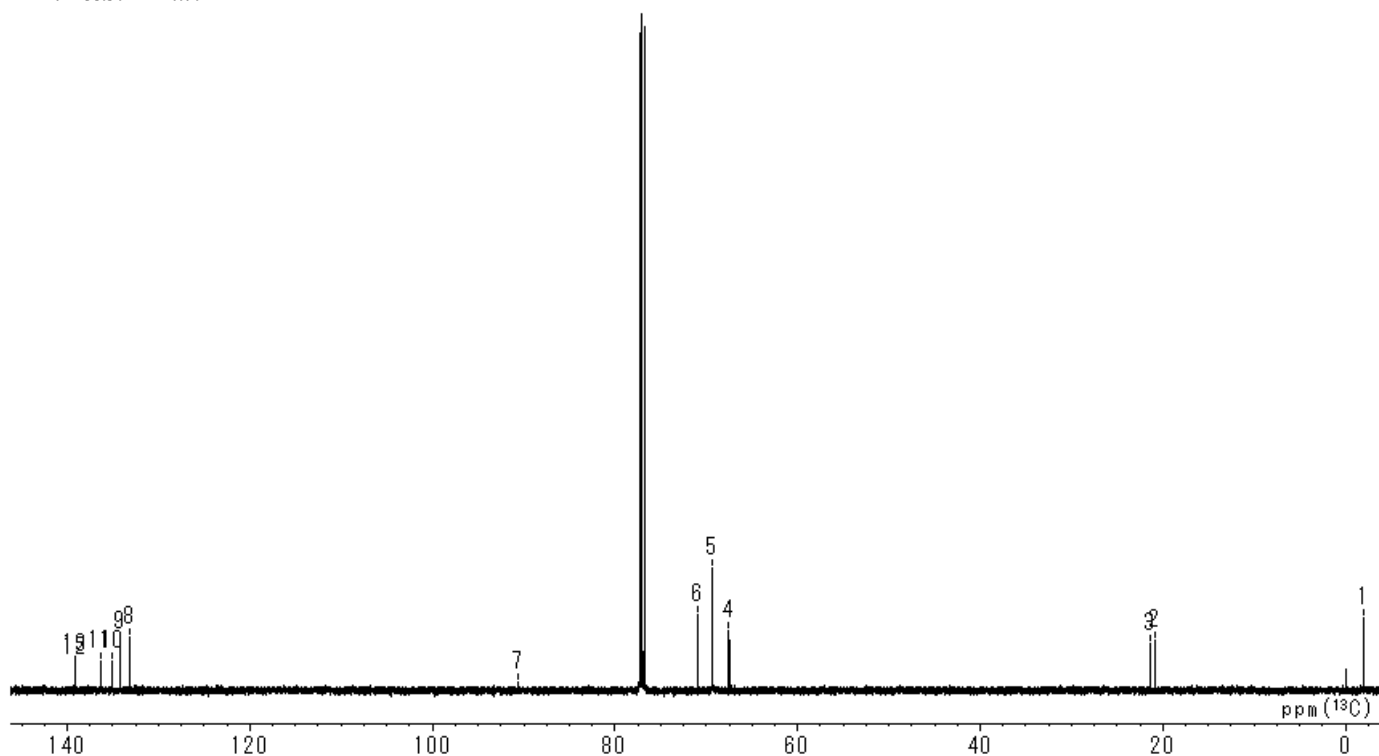


No.	δ /ppm	Height	No.	δ /ppm	Height
1	0.04	68.85	8	4.43	5.32
2	0.04	73.51	9	4.45	23.07
3	2.31	53.35	10	7.08	9.91
4	2.89	56.58	11	7.17	9.30
5	4.16	98.64			
6	4.34	19.83			
7	4.43	2.25			

No.	Start (ppm)	End (ppm)	Integral
1	0.0912	0.0200	5.9346
2	2.3650	2.2754	3.0753
3	2.9417	2.8158	3.0748
4	4.1799	4.1036	5.0731
5	4.3707	4.3134	2.064
6	4.4773	4.3957	2.9765
7	7.1010	7.0353	1.0287
8	7.1883	7.1369	1.0

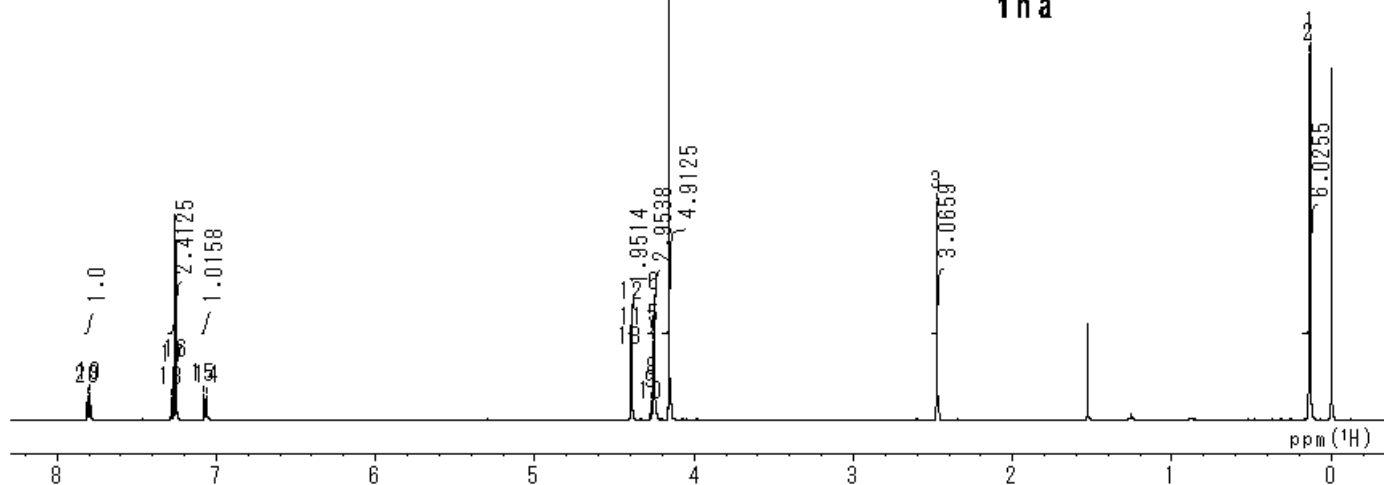
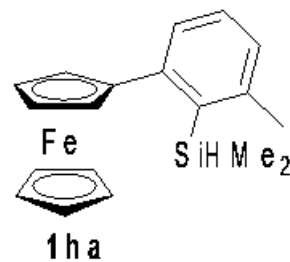


No.	δ /ppm	Height	No.	δ /ppm	Height
1	-2.03	10.76	8	133.10	7.96
2	20.90	7.42	9	134.19	7.07
3	21.43	6.91	10	135.11	4.21
4	67.51	8.89	11	136.35	4.37
5	69.35	18.12	12	139.05	3.41
6	70.90	11.12	13	139.18	3.74
7	90.64	1.11			

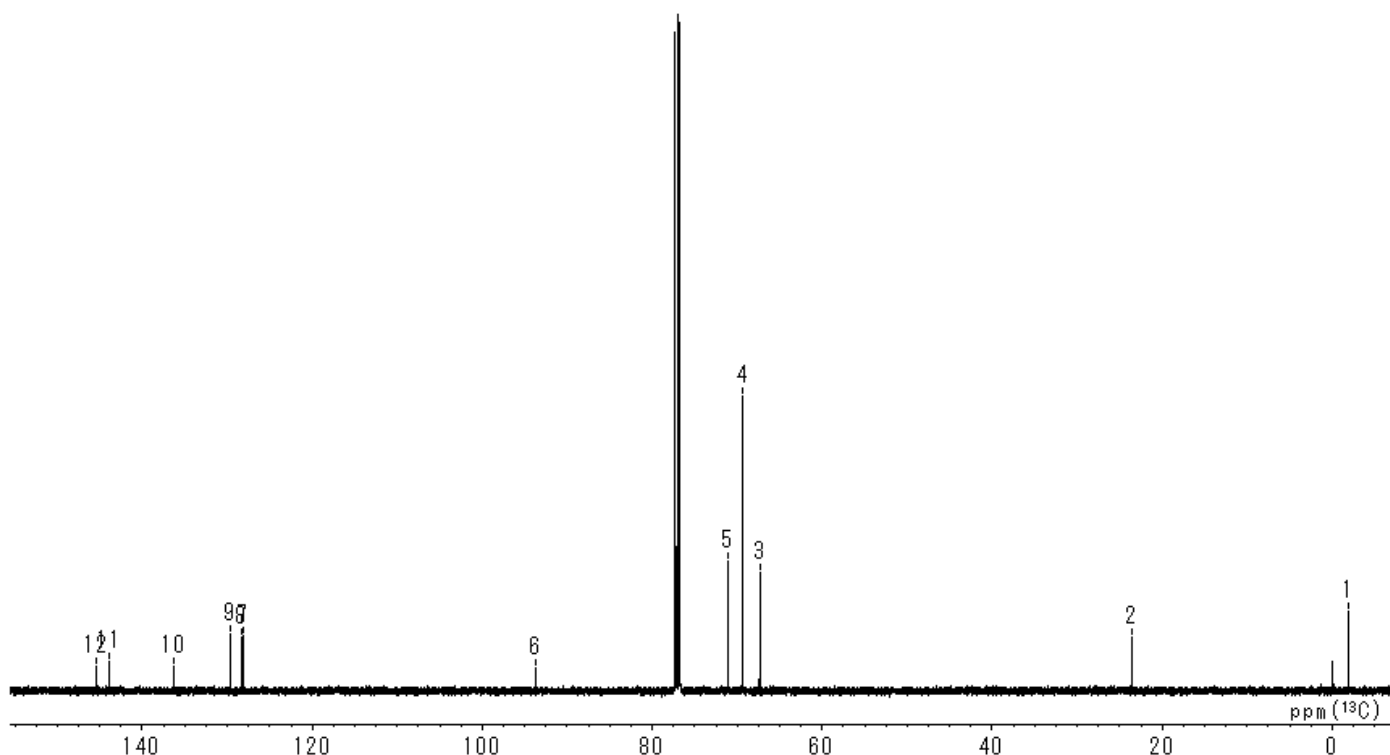


No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height
1	0.13	55.84	8	4.26	4.83	15	7.08	3.87
2	0.14	54.18	9	4.27	2.95	16	7.25	7.46
3	2.48	32.33	10	4.27	1.14	17	7.27	6.73
4	4.16	99.19	11	4.39	12.10	18	7.28	3.24
5	4.25	12.67	12	4.39	15.90	19	7.79	3.92
6	4.25	17.26	13	4.40	9.27	20	7.81	3.54
7	4.25	11.61	14	7.06	3.52			

No.	Start (ppm)	End (ppm)	Integral
1	0.1827	0.0794	6.0255
2	2.5071	2.4292	3.0659
3	4.1974	4.0451	4.9125
4	4.2855	4.2103	2.9538
5	4.4105	4.3645	1.9514
6	7.0907	7.0286	1.0158
7	7.2972	7.2102	2.4125
8	7.8236	7.7648	1.0

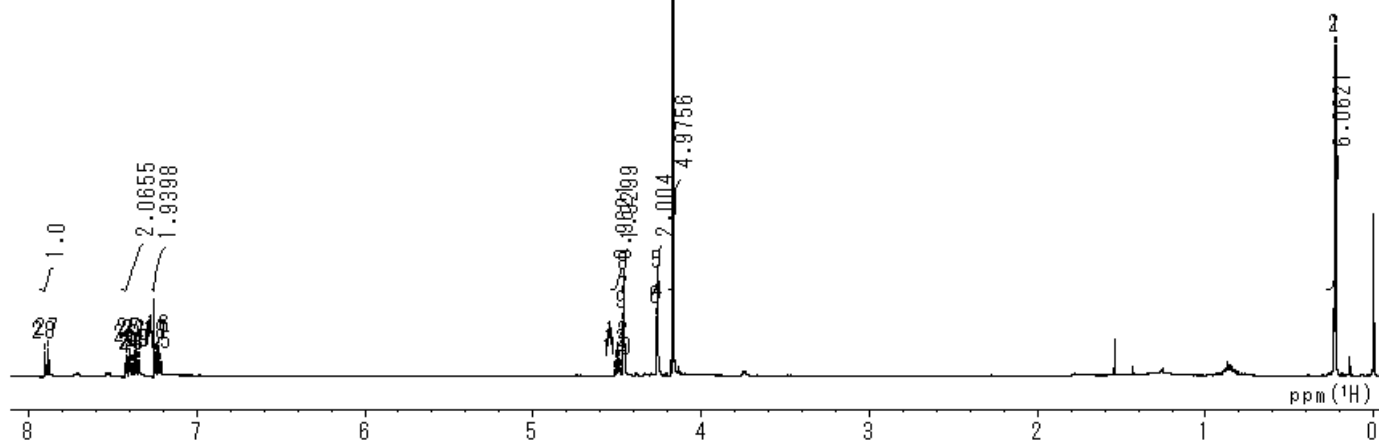
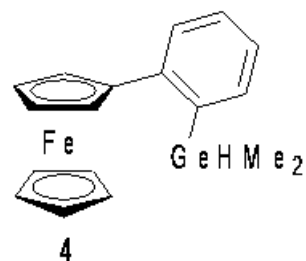


No.	δ /ppm	Height	No.	δ /ppm	Height
1	-1.91	11.57	8	128.31	7.78
2	29.55	7.94	9	129.64	8.34
3	67.36	17.42	10	136.33	3.55
4	69.42	43.15	11	143.95	4.25
5	71.09	19.07	12	145.42	3.62
6	93.74	3.33			
7	128.12	8.12			

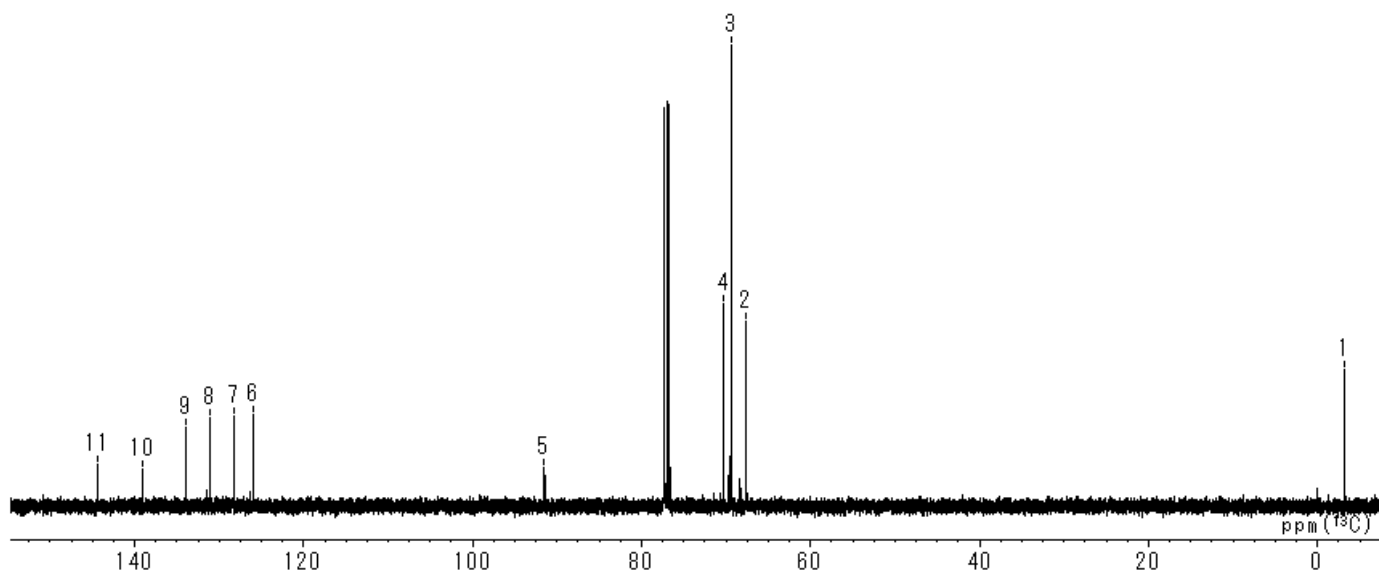


No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height
1	0.23	59.29	8	4.46	16.81	15	7.21	2.53	22	7.37	4.56
2	0.23	59.35	9	4.47	9.78	16	7.23	5.49	23	7.38	2.43
3	4.17	98.86	10	4.48	1.35	17	7.23	4.66	24	7.39	2.32
4	4.26	11.52	11	4.49	3.20	18	7.25	4.22	25	7.40	4.96
5	4.26	16.91	12	4.49	4.23	19	7.34	2.99	26	7.42	3.81
6	4.27	10.77	13	4.50	3.01	20	7.35	3.02	27	7.88	4.77
7	4.46	12.50	14	4.51	1.04	21	7.36	4.61	28	7.90	4.26

No.	Start (ppm)	End (ppm)	Integral
1	0.2776	0.2003	6.0621
2	4.1897	4.1158	4.9756
3	4.2763	4.2343	2.004
4	4.4702	4.4355	1.9299
5	4.5307	4.4702	0.9821
6	7.2635	7.1774	1.9398
7	7.4416	7.3096	2.0655
8	7.9300	7.8441	1.0

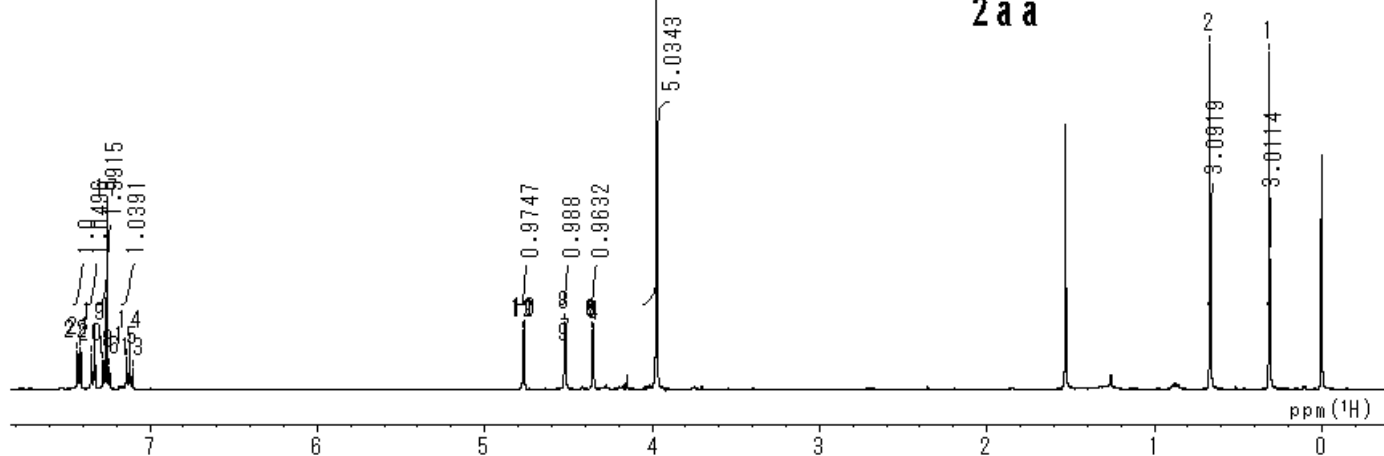
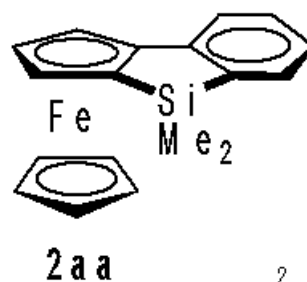


No.	δ /ppm	Height	No.	δ /ppm	Height
1	-3.12	29.53	8	131.02	19.00
2	67.71	40.10	9	134.00	16.93
3	69.44	99.99	10	139.07	7.98
4	70.36	43.85	11	144.40	9.09
5	91.49	8.29			
6	125.87	19.68			
7	128.26	19.32			

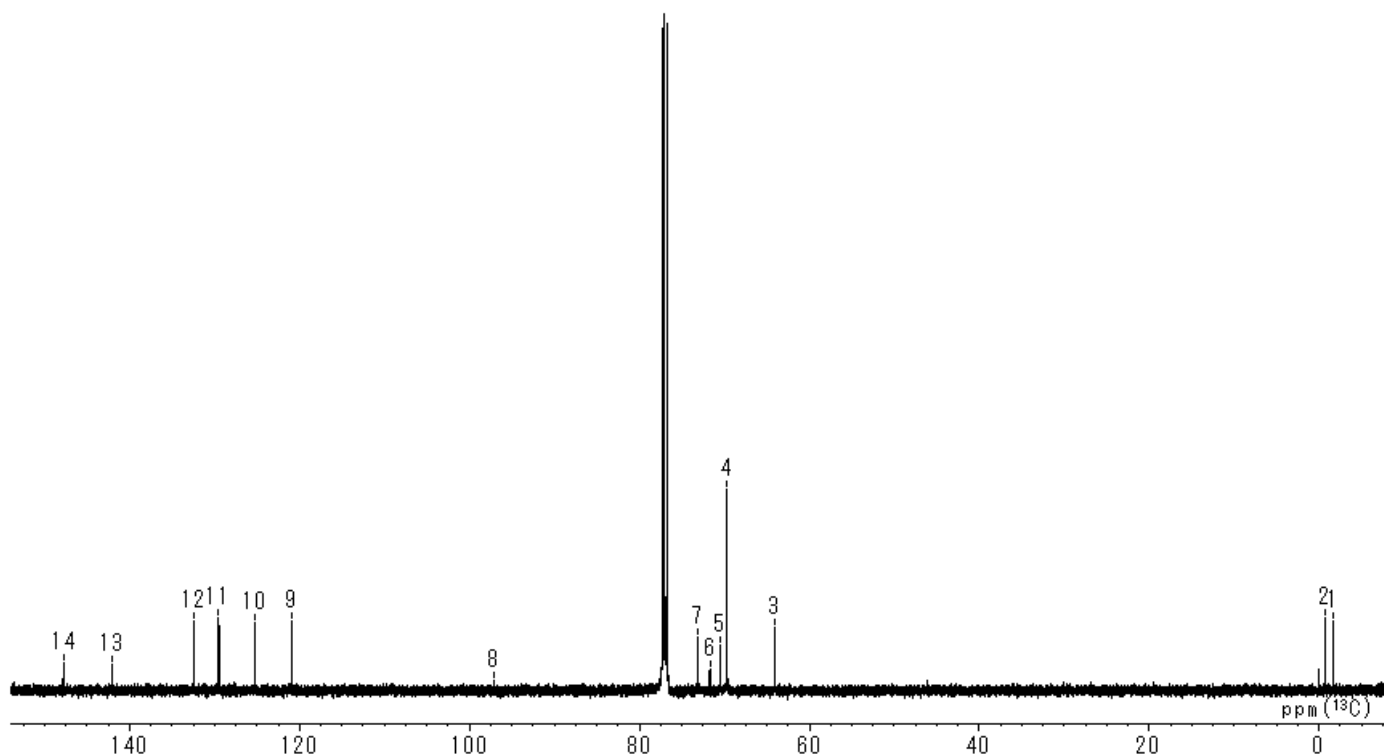


No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height
1	0.31	55.09	8	4.52	11.33	15	7.14	5.51	22	7.43	6.45
2	0.67	56.38	9	4.53	6.09	16	7.24	3.99			
3	3.98	96.54	10	4.76	10.08	17	7.26	29.41			
4	4.35	9.35	11	4.77	9.83	18	7.28	5.05			
5	4.35	9.63	12	4.77	9.96	19	7.33	9.38			
6	4.36	10.06	13	7.10	3.73	20	7.35	5.97			
7	4.51	6.74	14	7.12	8.19	21	7.42	7.11			

No.	Start (ppm)	End (ppm)	Integral
1	0.3262	0.3046	3.0114
2	0.6801	0.6472	3.0919
3	4.0522	3.8947	5.0343
4	4.3805	4.3224	0.9632
5	4.5475	4.4926	0.988
6	4.7973	4.7391	0.9747
7	7.1662	7.0880	1.0391
8	7.3080	7.2225	1.9915
9	7.3935	7.3080	1.0496
10	7.4603	7.3935	1.0

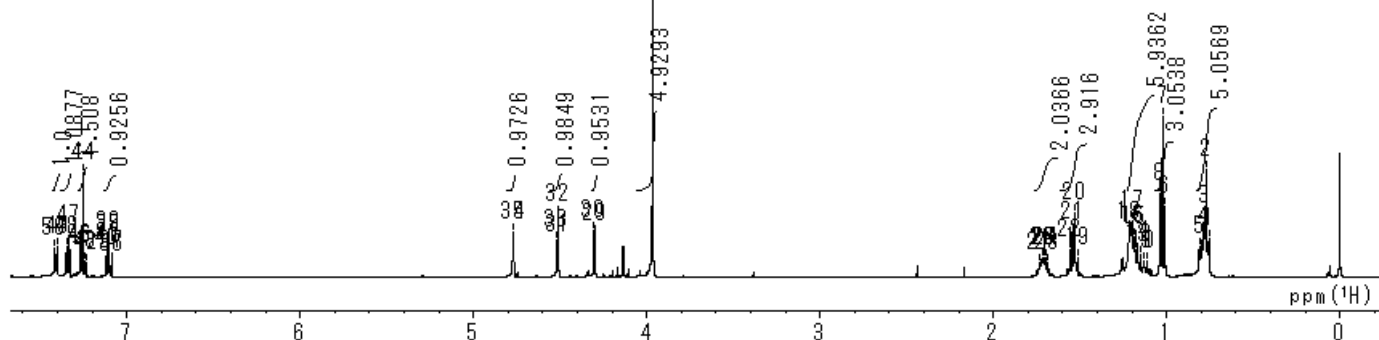
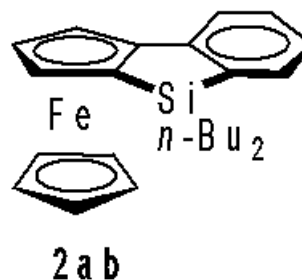


No.	δ /ppm	Height	No.	δ /ppm	Height
1	-1.61	10.20	8	97.03	1.51
2	-0.76	10.59	9	120.91	10.21
3	64.04	9.18	10	125.24	9.94
4	69.68	29.66	11	129.50	10.80
5	70.51	6.76	12	132.43	10.30
6	71.71	3.06	13	142.11	3.77
7	73.19	7.75	14	147.81	4.00

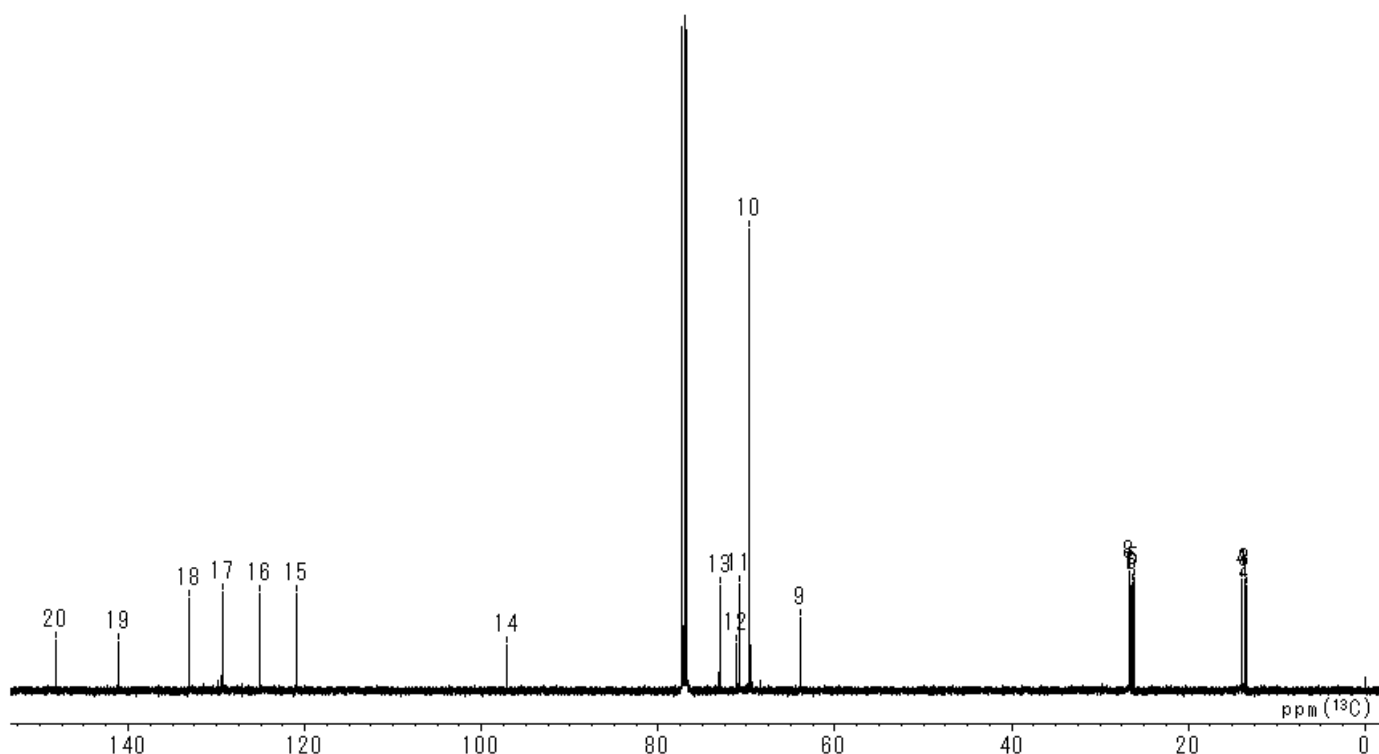


No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height
1	0.76	6.17	10	1.13	2.54	19	1.51	3.19	28	3.97	99.55	37	7.09	2.56	46	7.27	3.58
2	0.77	17.42	11	1.13	2.73	20	1.53	10.54	29	4.30	7.03	38	7.10	5.16	47	7.33	6.80
3	0.78	9.93	12	1.15	3.67	21	1.54	7.35	30	4.30	7.59	39	7.10	5.72	48	7.35	5.04
4	0.79	6.40	13	1.17	3.63	22	1.56	4.38	31	4.51	5.21	40	7.12	3.27	49	7.40	5.06
5	0.81	5.03	14	1.17	4.10	23	1.69	2.24	32	4.51	10.18	41	7.12	3.66	50	7.42	4.82
6	1.01	11.63	15	1.18	6.46	24	1.70	3.15	33	4.52	5.97	42	7.24	2.35			
7	1.02	26.07	16	1.19	6.73	25	1.71	3.10	34	4.77	7.26	43	7.24	2.74			
8	1.04	13.53	17	1.20	9.04	26	1.72	3.23	35	4.77	7.36	44	7.25	16.87			
9	1.11	2.71	18	1.21	7.28	27	1.73	2.24	36	7.09	2.19	45	7.27	3.35			

No.	Start (ppm)	End (ppm)	Integral
1	0.8261	0.7030	5.0569
2	1.0687	0.9569	3.0538
3	1.2271	1.0687	5.9362
4	1.6091	1.4573	2.916
5	1.7594	1.6215	2.0366
6	4.0591	3.9341	4.9293
7	4.3209	4.2794	0.9531
8	4.5557	4.4809	0.9849
9	4.8113	4.7552	0.9726
10	7.1341	7.0606	0.9256
11	7.2826	7.2286	1.508
12	7.3853	7.3168	1.0877
13	7.4327	7.3853	1.0

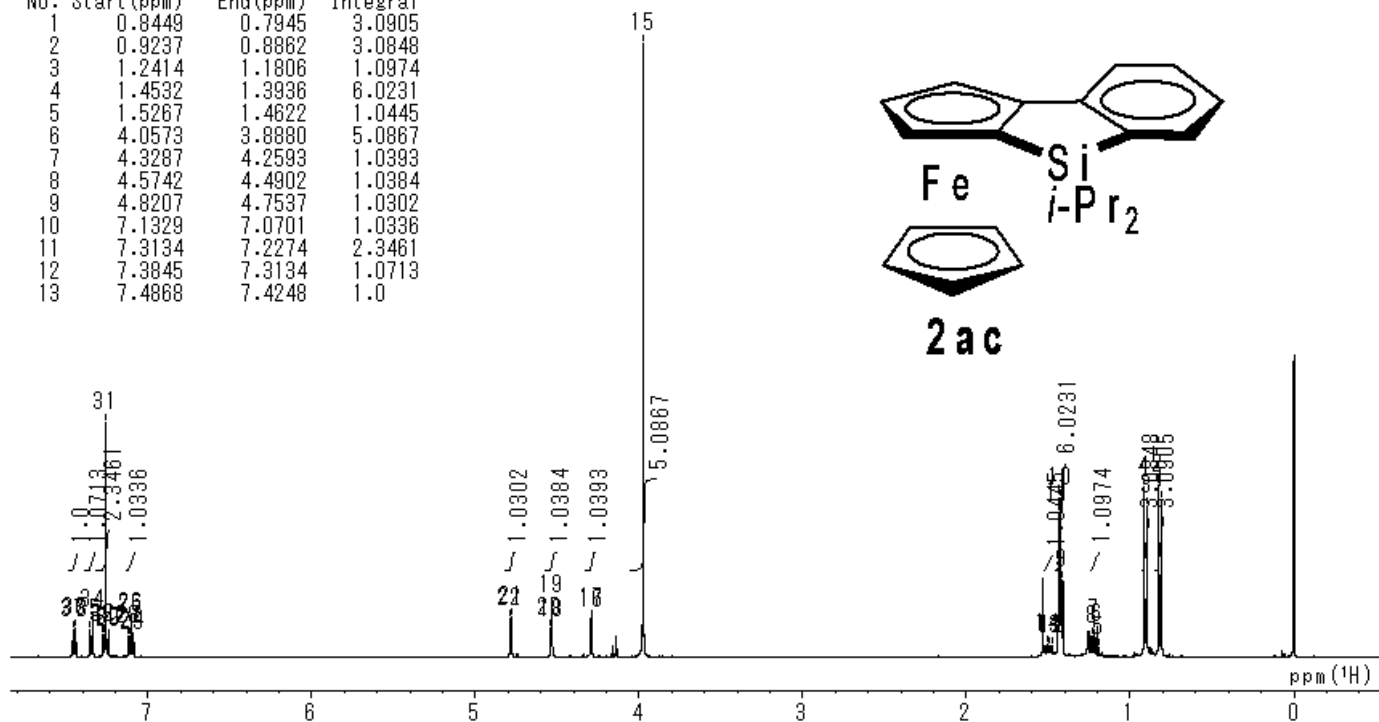
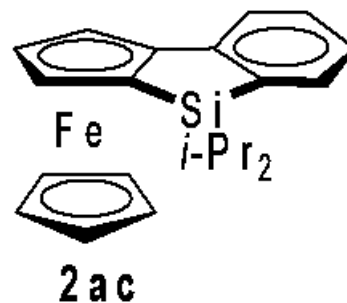


No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height
1	13.35	15.55	8	26.70	17.62	15	120.96	14.23
2	13.52	14.86	9	63.86	10.60	16	125.04	14.33
3	13.66	16.32	10	69.64	68.20	17	129.37	14.57
4	13.99	16.44	11	70.87	15.79	18	133.08	13.59
5	26.17	16.62	12	71.22	6.87	19	141.03	7.02
6	26.27	15.95	13	73.06	15.33	20	148.19	7.35
7	26.58	15.90	14	97.11	6.70			

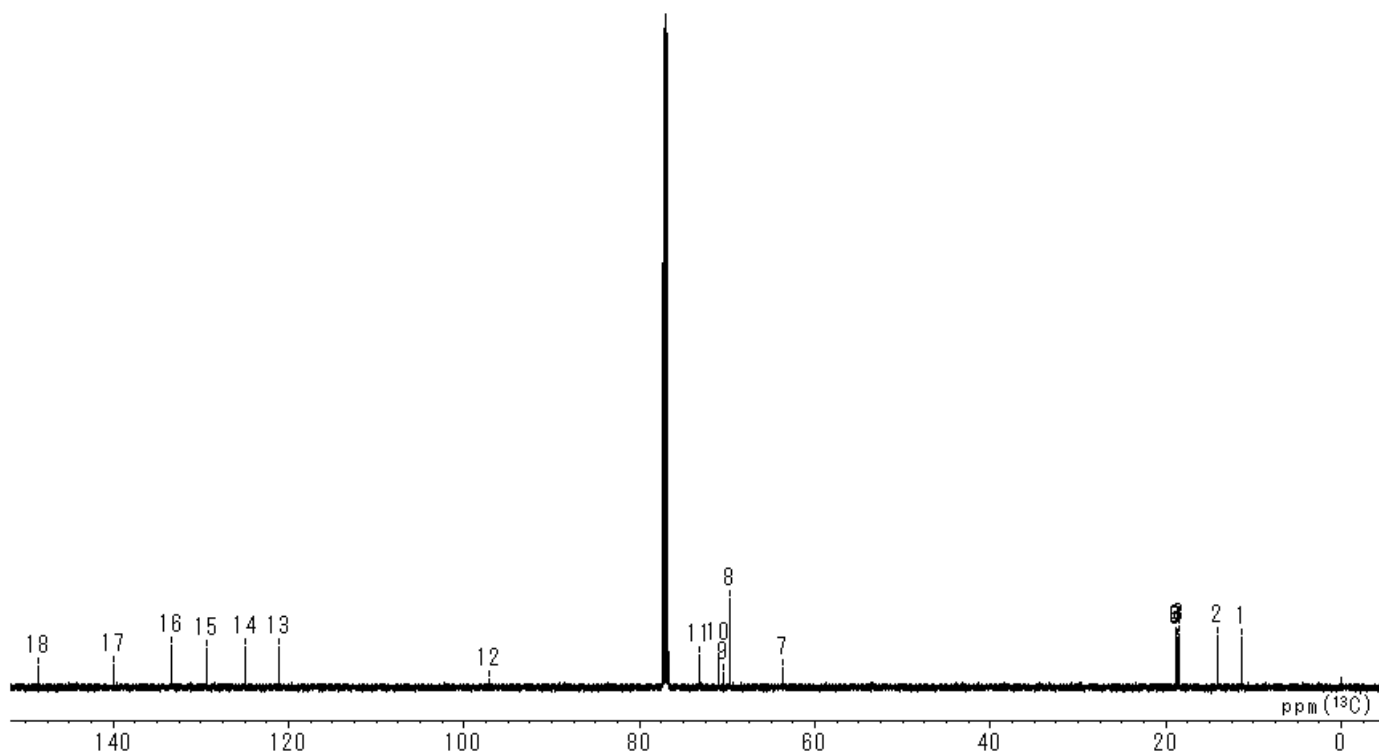


No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height
1	0.81	25.69	8	1.24	3.33	15	3.98	99.97	22	4.78	6.39	29	7.24	2.79	36	7.44	4.73
2	0.82	28.09	9	1.41	12.67	16	4.29	6.00	23	7.09	2.47	30	7.24	3.05	37	7.46	4.37
3	0.90	24.50	10	1.43	25.86	17	4.29	6.35	24	7.09	2.69	31	7.26	38.11			
4	0.91	27.81	11	1.44	23.55	18	4.53	4.50	25	7.10	5.32	32	7.27	3.57			
5	1.19	1.66	12	1.48	1.81	19	4.53	8.44	26	7.10	5.58	33	7.27	3.55			
6	1.21	3.61	13	1.49	1.90	20	4.54	4.79	27	7.12	3.34	34	7.34	5.92			
7	1.22	4.45	14	1.51	1.98	21	4.78	6.51	28	7.12	3.50	35	7.35	4.33			

No.	Start (ppm)	End (ppm)	Integral
1	0.8449	0.7945	3.0905
2	0.9237	0.8862	3.0848
3	1.2414	1.1806	1.0974
4	1.4532	1.3936	6.0231
5	1.5267	1.4622	1.0445
6	4.0573	3.8880	5.0867
7	4.3287	4.2593	1.0393
8	4.5742	4.4902	1.0384
9	4.8207	4.7537	1.0302
10	7.1329	7.0701	1.0336
11	7.3134	7.2274	2.3461
12	7.3845	7.3134	1.0713
13	7.4868	7.4248	1.0

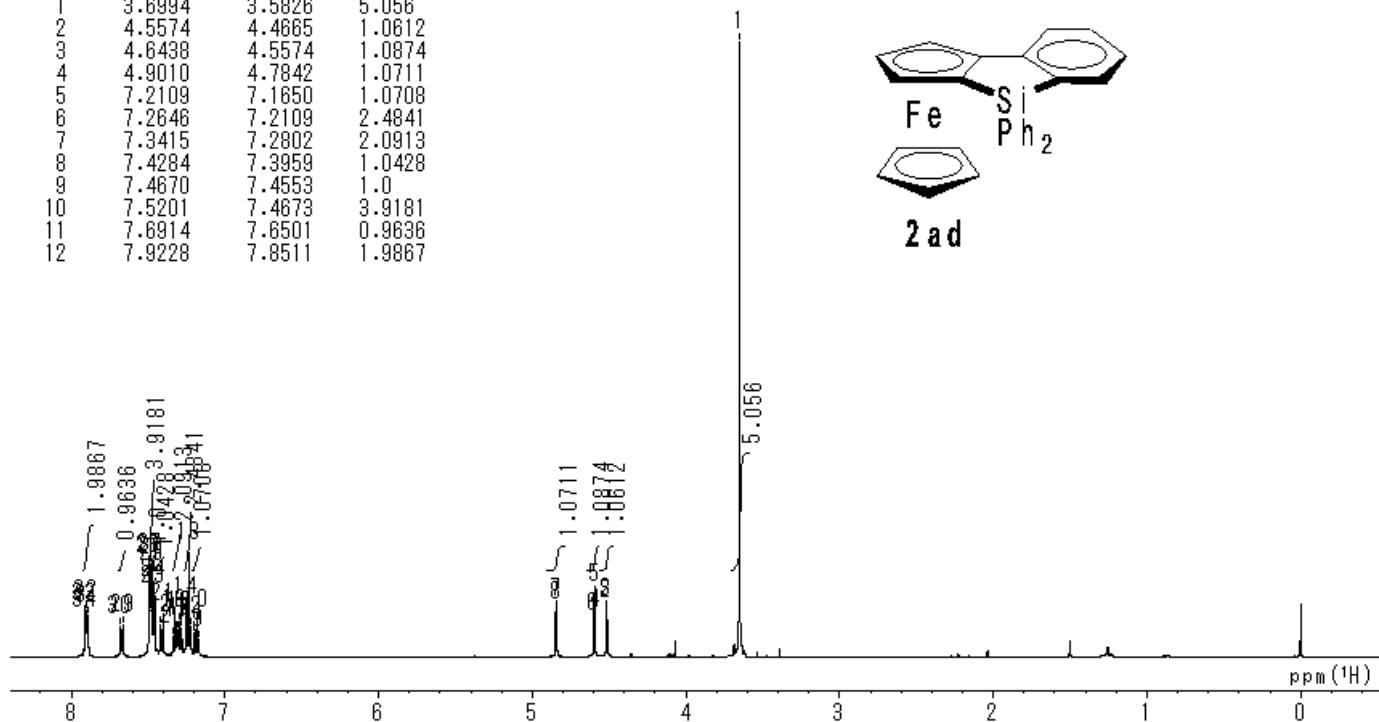
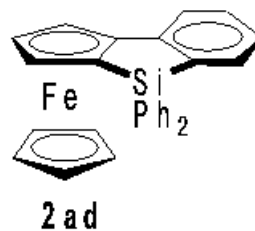


No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height
1	11.26	7.37	8	69.71	13.17	15	129.33	5.69
2	14.03	7.67	9	70.45	2.05	16	133.42	6.16
3	18.41	7.87	10	70.96	4.92	17	139.89	3.25
4	18.70	7.25	11	73.09	4.69	18	148.53	3.03
5	18.77	7.30	12	97.21	1.21			
6	18.88	7.51	13	121.05	5.92			
7	63.73	2.78	14	124.97	5.90			

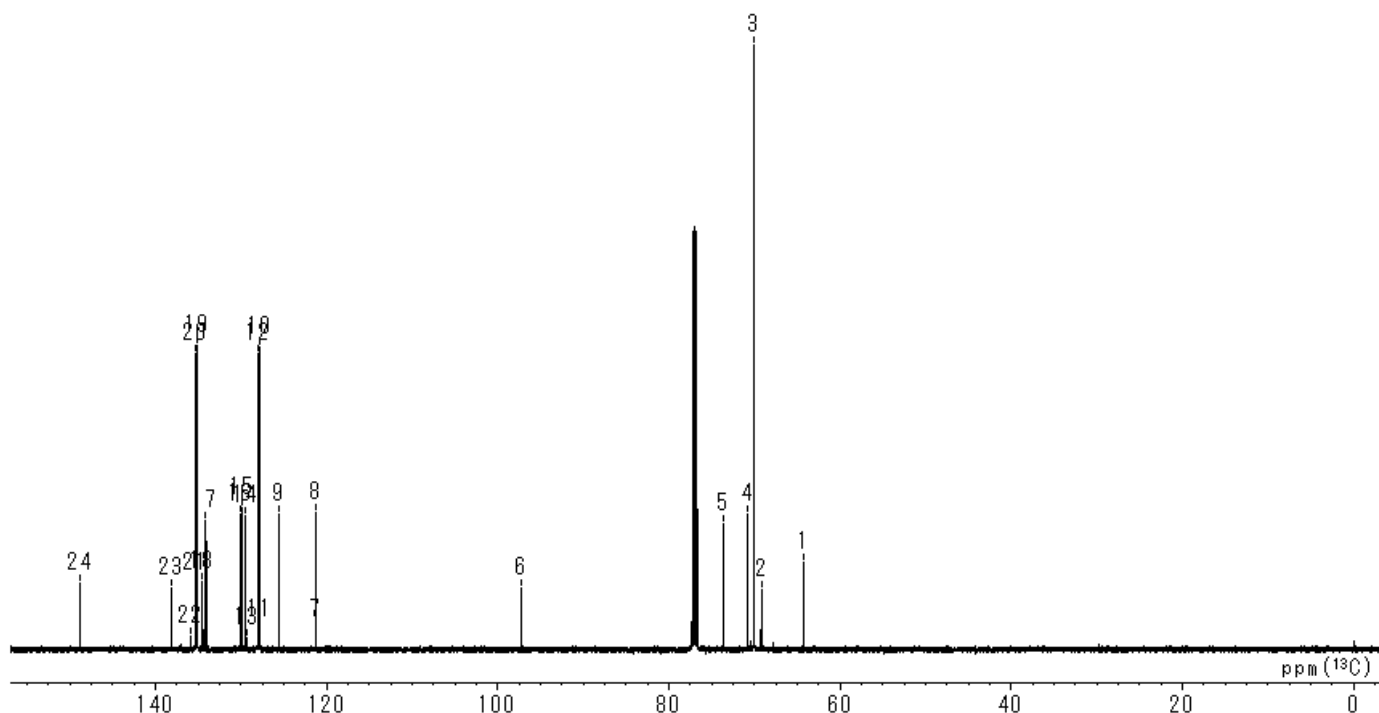


No.	δ/ppm	Height	No.	δ/ppm	Height	No.	δ/ppm	Height	No.	δ/ppm	Height	No.	δ/ppm	Height
1	3.65	100.00	8	4.85	7.30	15	7.28	4.72	22	7.42	5.24	29	7.67	5.31
2	4.51	7.50	9	7.17	2.99	16	7.30	5.74	23	7.46	10.06	30	7.68	4.88
3	4.52	7.80	10	7.18	6.04	17	7.31	4.36	24	7.46	11.05	31	7.89	6.74
4	4.59	5.92	11	7.20	3.79	18	7.32	5.96	25	7.47	13.63	32	7.90	7.68
5	4.60	10.18	12	7.22	4.89	19	7.32	6.08	26	7.48	14.54	33	7.91	7.14
6	4.60	5.38	13	7.24	17.08	20	7.34	3.39	27	7.49	15.05	34	7.91	5.91
7	4.84	7.96	14	7.25	7.98	21	7.40	7.12	28	7.49	14.99			

No.	Start (ppm)	End (ppm)	Integral
1	3.6994	3.5826	5.056
2	4.5574	4.4665	1.0612
3	4.6438	4.5574	1.0874
4	4.9010	4.7842	1.0711
5	7.2109	7.1650	1.0708
6	7.2646	7.2109	2.4841
7	7.3415	7.2802	2.0913
8	7.4284	7.3959	1.0428
9	7.4670	7.4553	1.0
10	7.5201	7.4673	3.9181
11	7.6914	7.6501	0.9636
12	7.9228	7.8511	1.9867

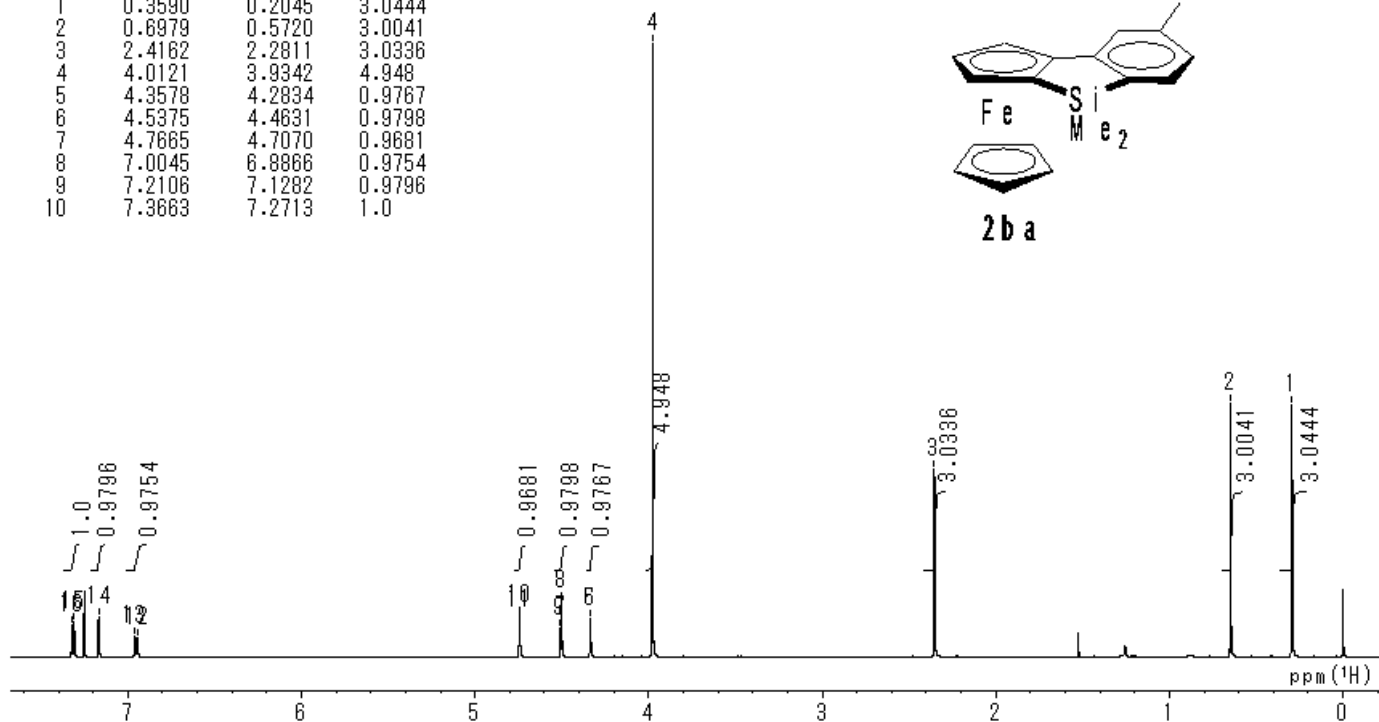
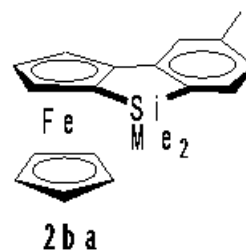


No.	δ/ppm	Height	No.	δ/ppm	Height	No.	δ/ppm	Height	No.	δ/ppm	Height
1	64.32	14.15	8	121.30	22.24	15	129.93	22.88	22	135.83	2.20
2	69.08	9.66	9	125.58	21.84	16	130.11	21.94	23	138.12	10.04
3	70.10	98.23	10	127.81	49.25	17	134.13	20.90	24	148.86	10.61
4	70.81	22.06	11	127.85	3.13	18	134.50	10.89			
5	73.68	20.32	12	128.06	48.16	19	135.10	49.36			
6	97.31	10.01	13	129.43	1.89	20	135.25	48.10			
7	121.29	3.15	14	129.56	21.82	21	135.31	10.80			

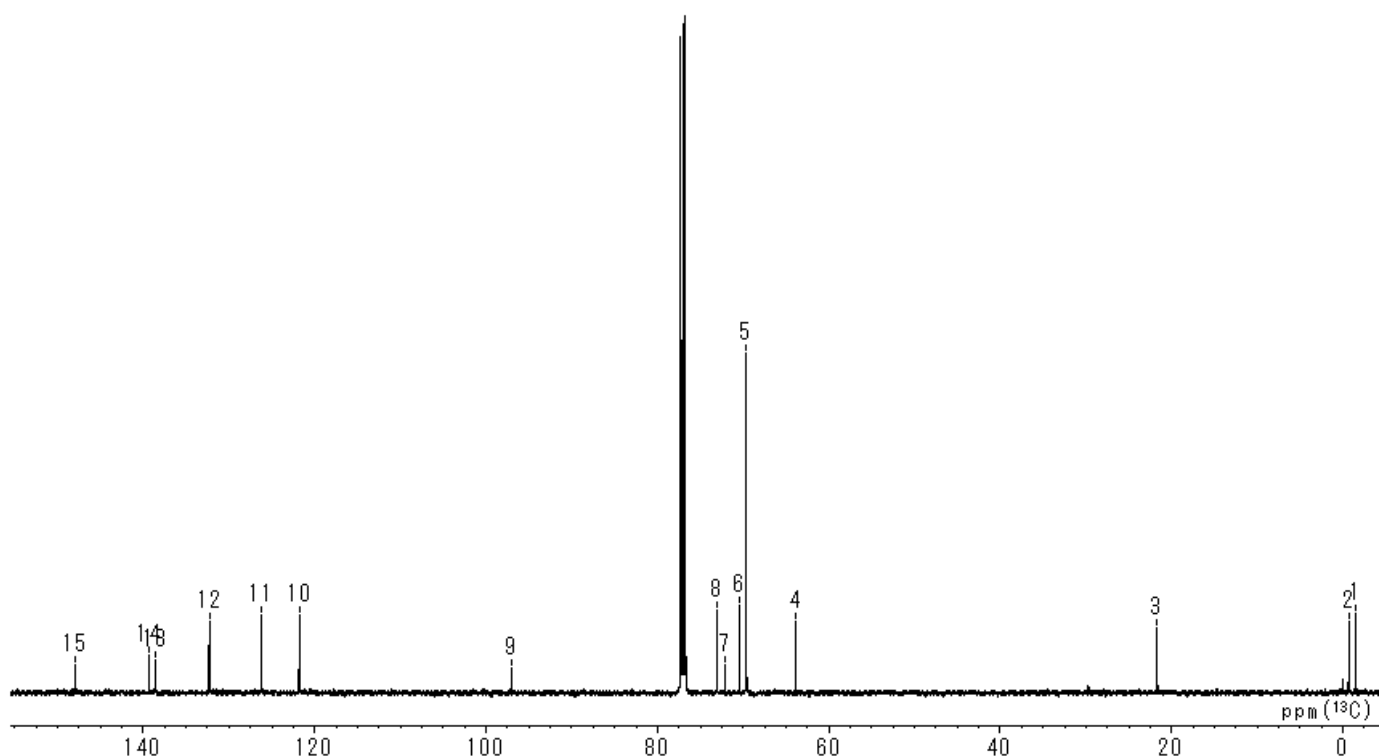


No.	δ/ppm	Height	No.	δ/ppm	Height	No.	δ/ppm	Height
1	0.29	40.98	8	4.50	9.05	15	7.31	5.81
2	0.65	41.17	9	4.51	4.70	16	7.32	5.35
3	2.35	30.54	10	4.74	6.75			
4	3.98	99.78	11	4.75	6.00			
5	4.33	6.34	12	6.94	3.13			
6	4.34	6.21	13	6.96	3.43			
7	4.50	5.00	14	7.17	6.51			

No.	Start (ppm)	End (ppm)	Integral
1	0.3590	0.2045	3.0444
2	0.6979	0.5720	3.0041
3	2.4162	2.2811	3.0336
4	4.0121	3.9342	4.948
5	4.3578	4.2834	0.9767
6	4.5375	4.4631	0.9798
7	4.7665	4.7070	0.9681
8	7.0045	6.8866	0.9754
9	7.2106	7.1282	0.9796
10	7.3663	7.2713	1.0

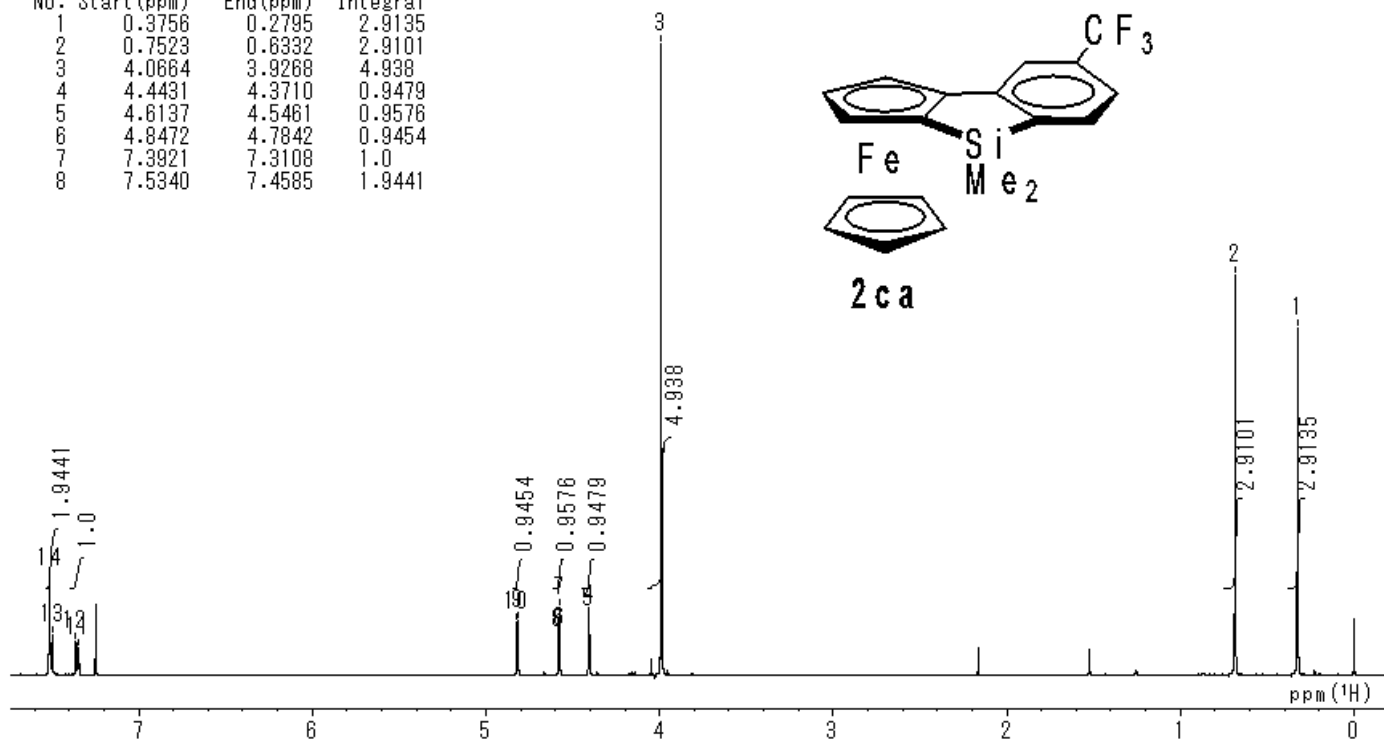
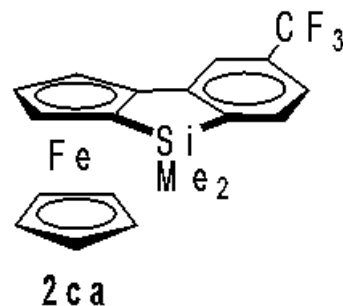


No.	δ/ppm	Height	No.	δ/ppm	Height	No.	δ/ppm	Height
1	-1.52	11.60	8	73.04	12.20	15	148.01	4.05
2	-0.66	10.56	9	97.07	3.55			
3	21.68	9.41	10	121.81	11.47			
4	63.88	10.34	11	126.21	11.33			
5	69.64	50.12	12	132.30	10.50			
6	70.42	12.88	13	138.58	4.73			
7	72.10	3.96	14	139.31	5.41			

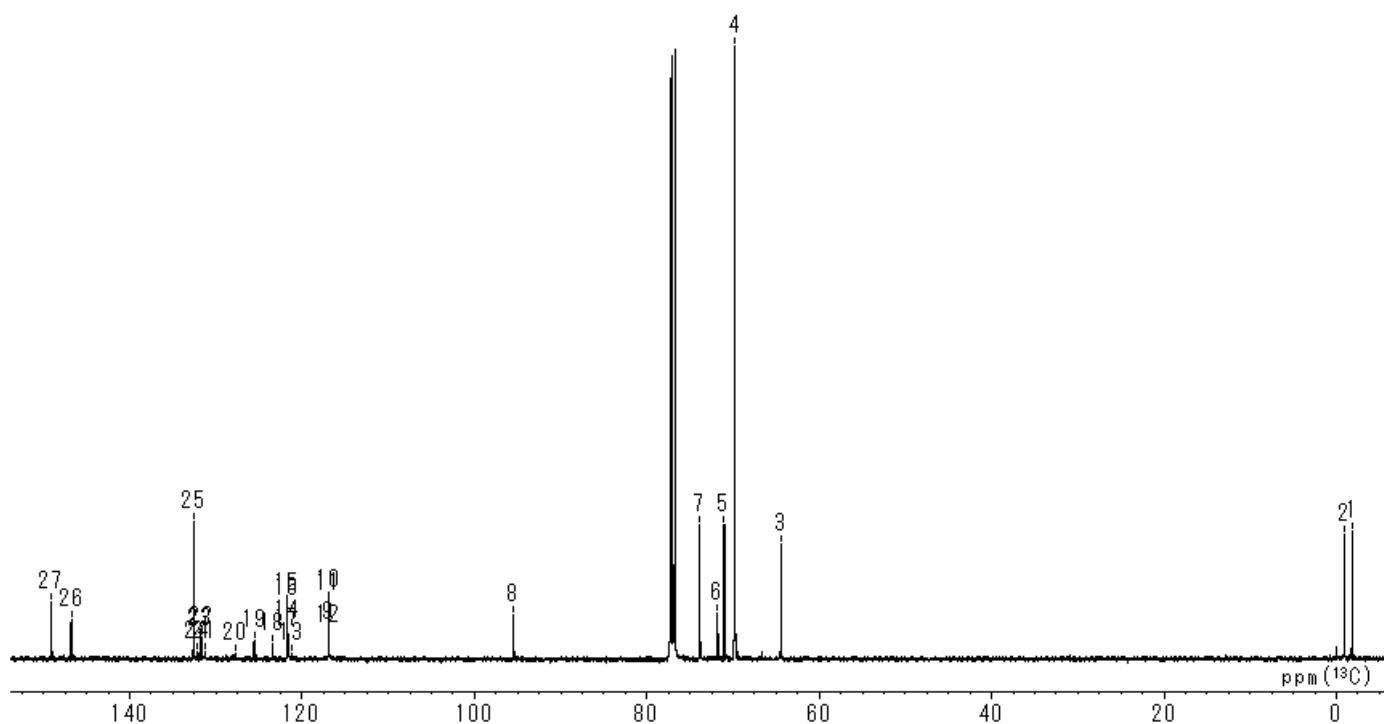


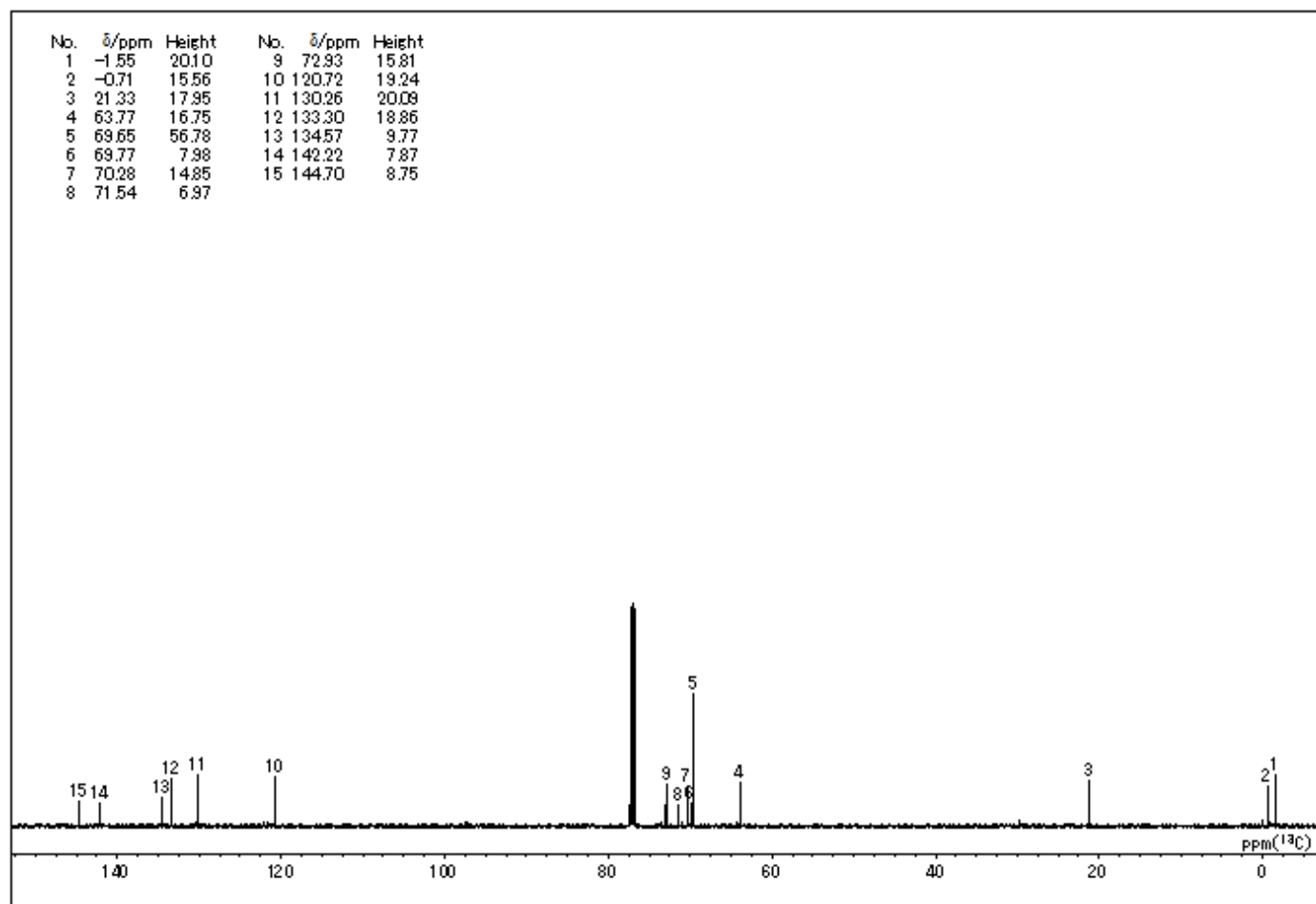
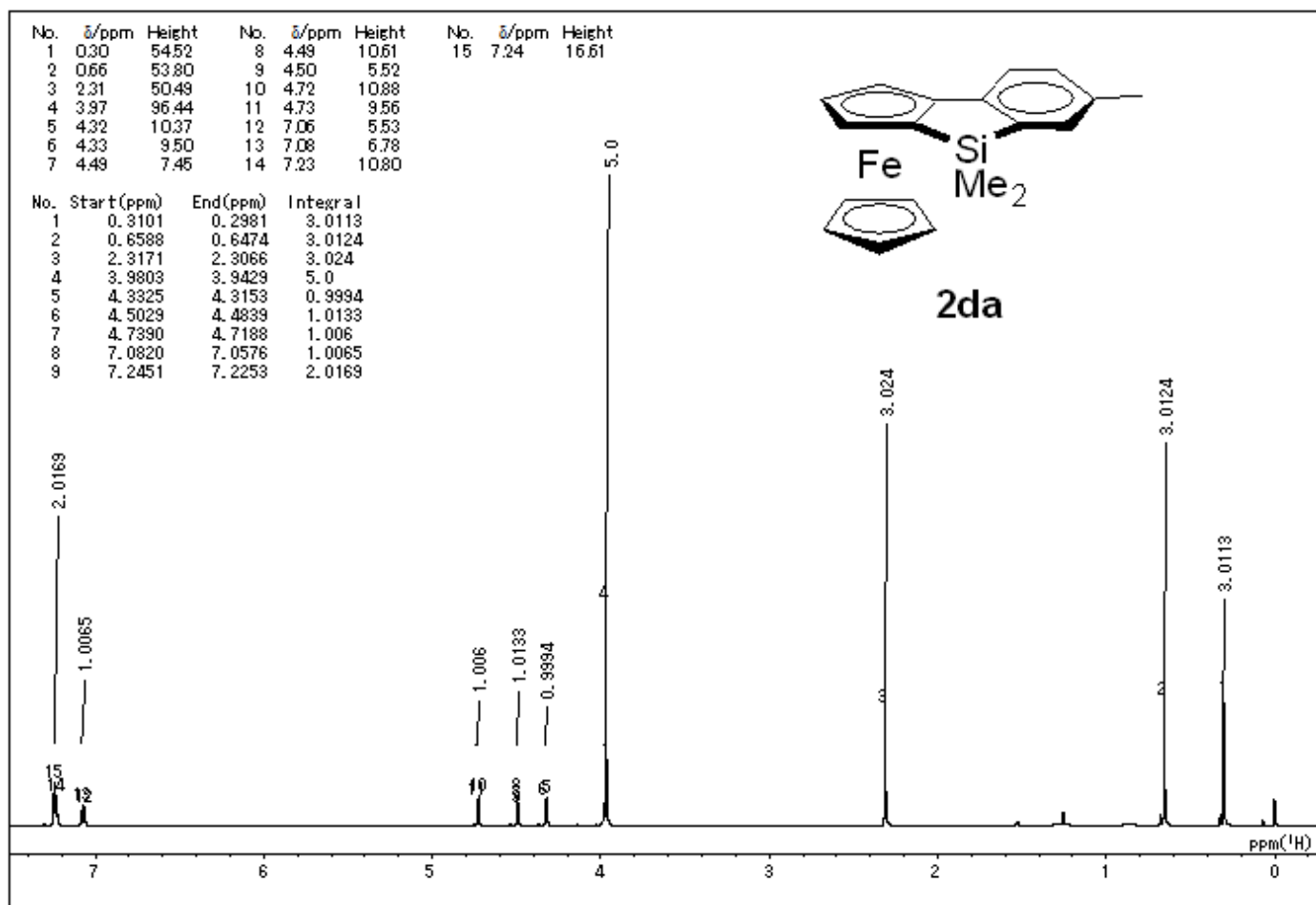
No.	δ /ppm	Height	No.	δ /ppm	Height
1	0.33	46.70	8	4.58	4.74
2	0.69	53.80	9	4.82	7.25
3	3.99	84.82	10	4.82	7.03
4	4.41	8.00	11	7.35	3.69
5	4.41	7.67	12	7.36	4.50
6	4.57	5.00	13	7.50	5.49
7	4.58	8.97	14	7.51	12.91

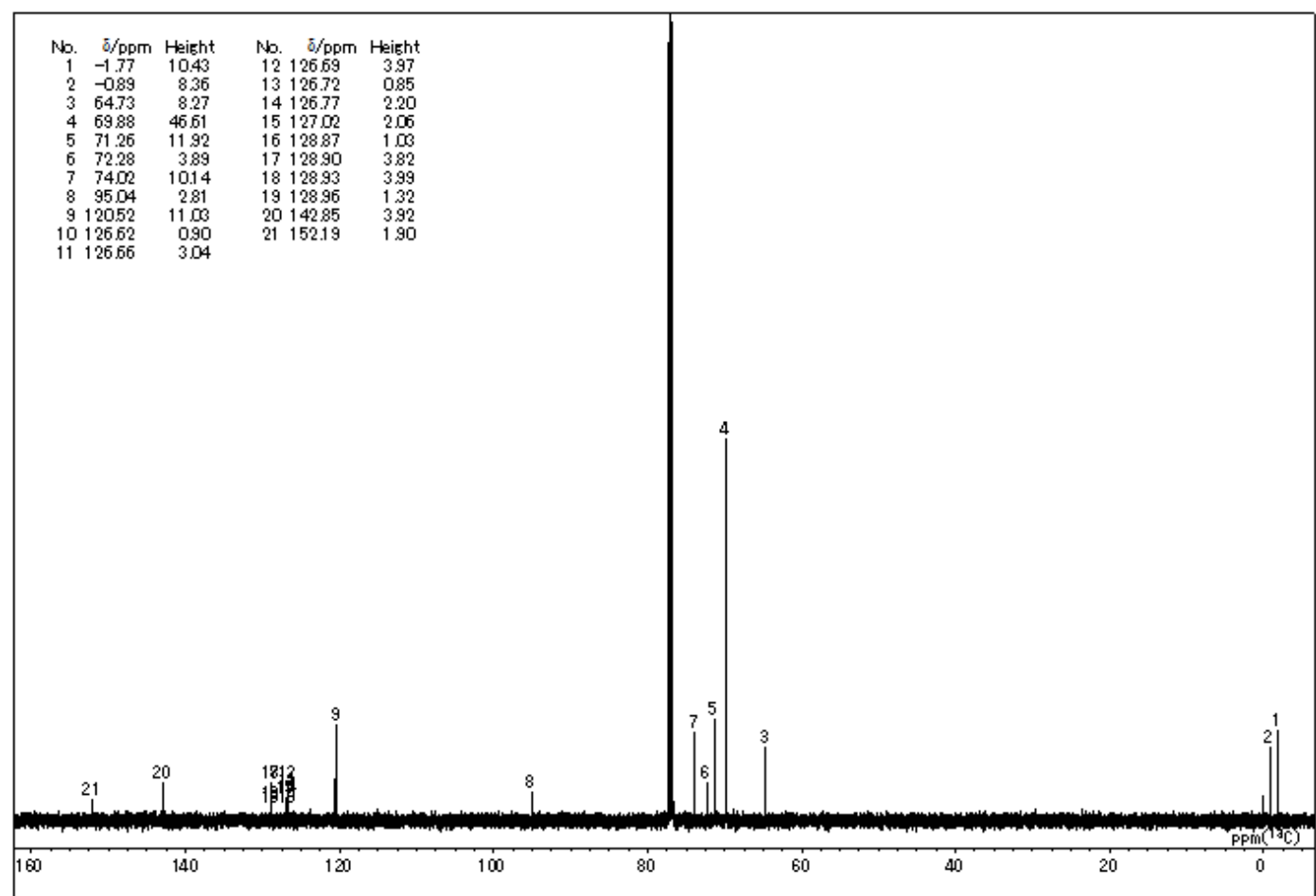
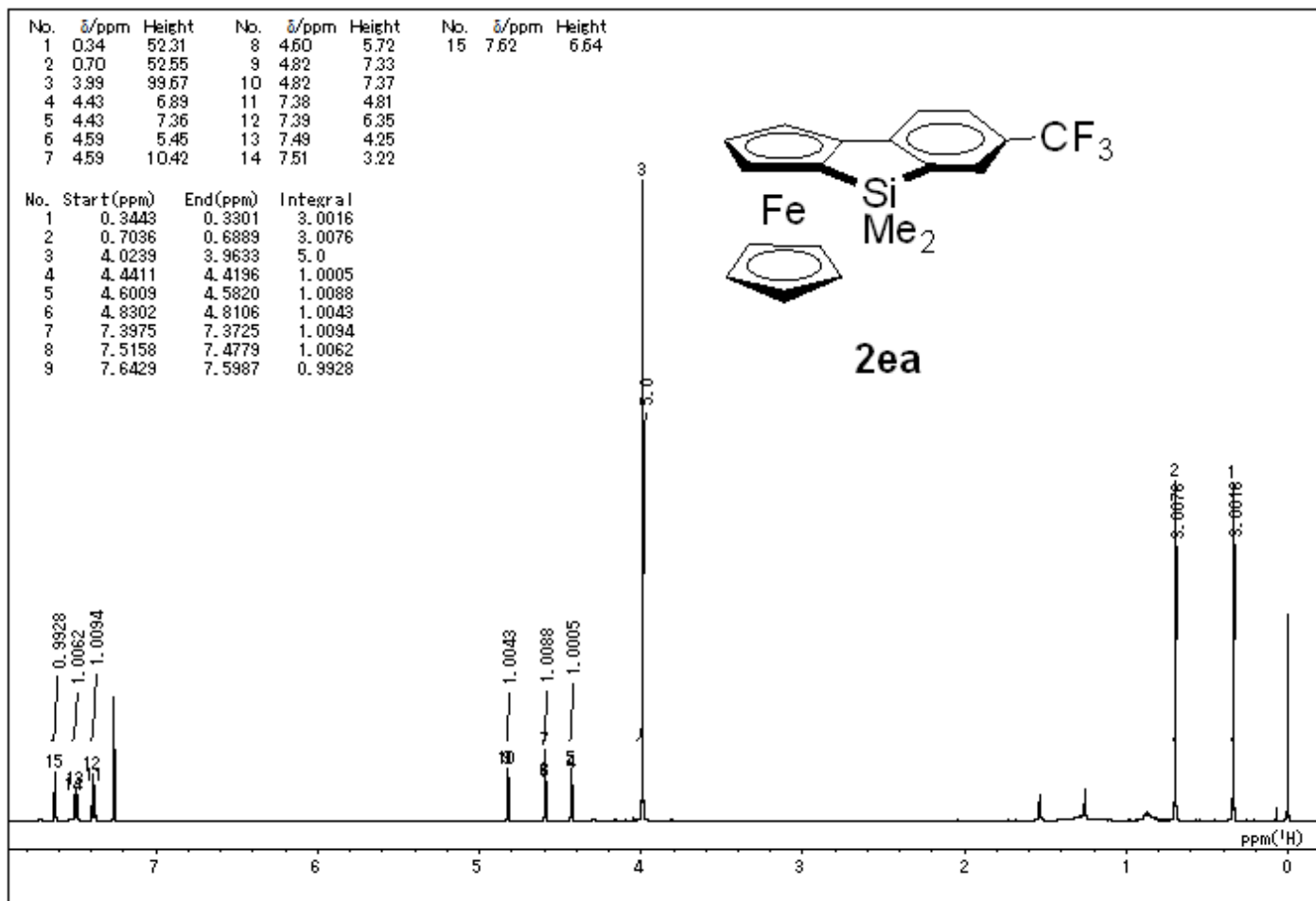
No.	Start (ppm)	End (ppm)	Integral
1	0.3756	0.2795	2.9135
2	0.7523	0.6332	2.9101
3	4.0664	3.9268	4.938
4	4.4431	4.3710	0.9479
5	4.6137	4.5461	0.9576
6	4.8472	4.7842	0.9454
7	7.3921	7.3108	1.0
8	7.5340	7.4585	1.9441



No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height
1	-1.81	20.74	8	95.43	7.11	15	121.69	8.95	22	131.58	3.31
2	-0.95	20.21	9	116.87	4.29	16	121.72	8.01	23	131.83	3.18
3	64.45	18.47	10	116.89	9.48	17	121.76	3.17	24	132.09	0.99
4	69.84	99.67	11	116.92	8.97	18	123.38	2.44	25	132.61	22.19
5	71.02	21.78	12	116.95	3.79	19	125.57	2.79	26	146.79	6.16
6	71.78	7.36	13	121.20	0.89	20	127.76	0.66	27	149.06	9.20
7	73.85	21.62	14	121.67	4.32	21	131.33	1.06			

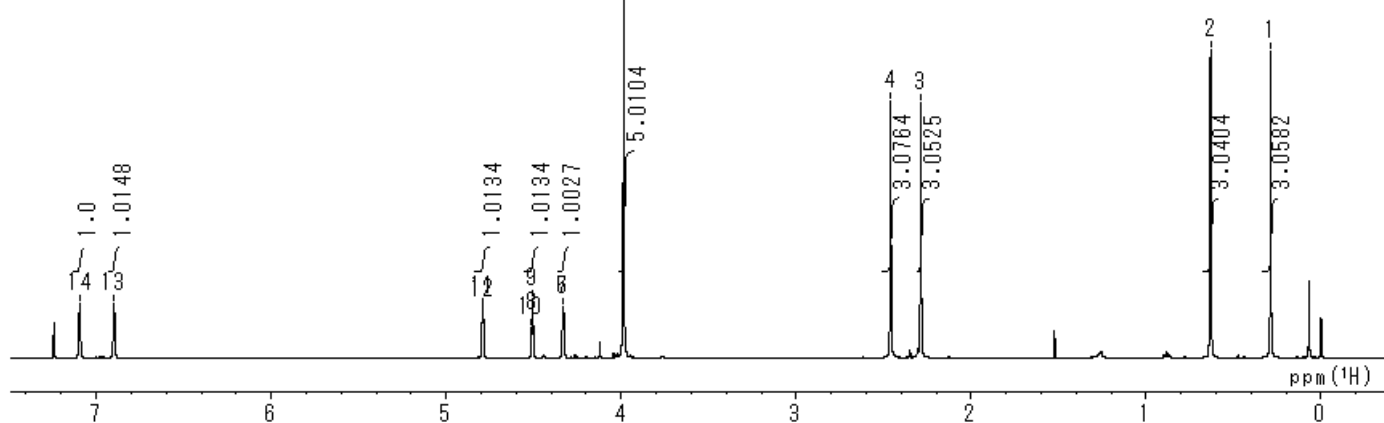
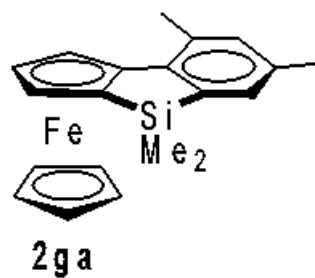




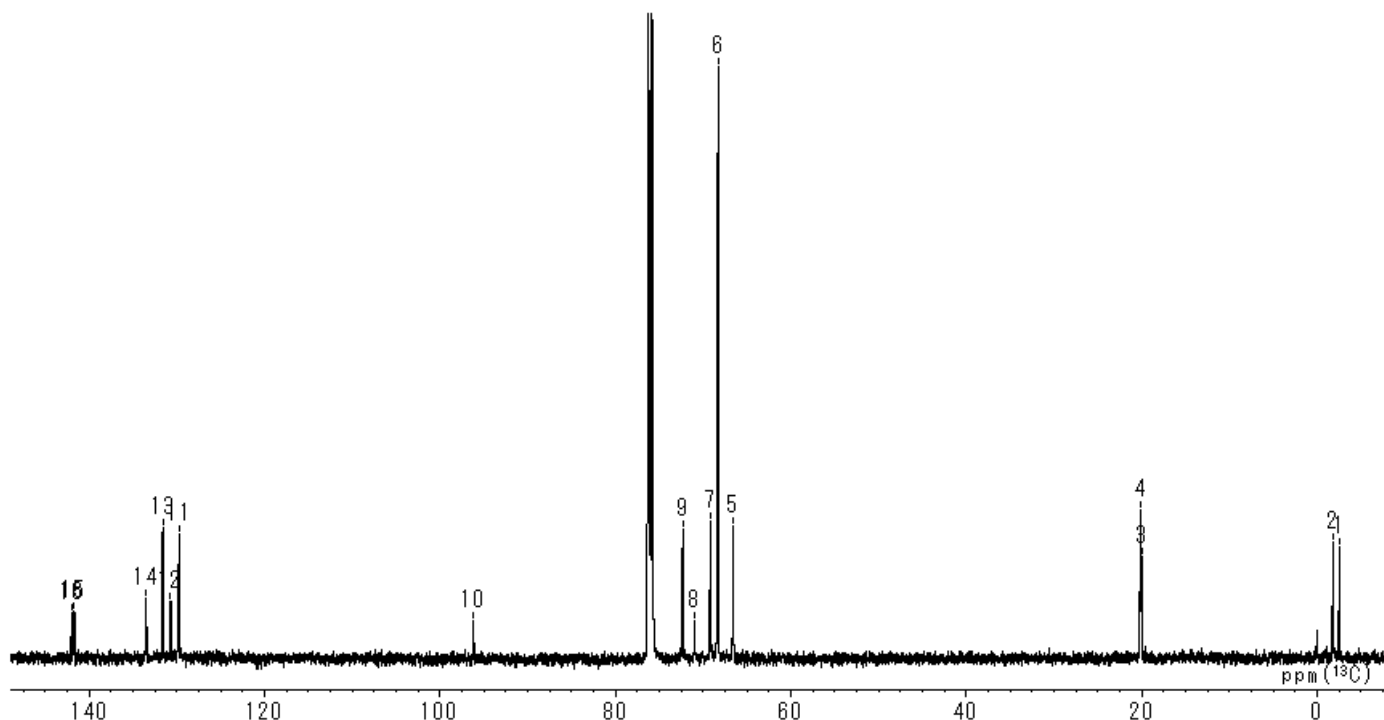


No.	δ /ppm	Height	No.	δ /ppm	Height
1	0.29	49.82	8	4.50	5.78
2	0.63	50.17	9	4.51	9.62
3	2.29	41.49	10	4.51	4.95
4	2.46	41.75	11	4.79	8.46
5	3.99	97.58	12	4.79	7.94
6	4.33	8.25	13	6.90	8.87
7	4.33	8.38	14	7.09	8.86

No.	Start (ppm)	End (ppm)	Integral
1	0.3373	0.2393	3.0582
2	0.6776	0.5803	3.0404
3	2.3042	2.2366	3.0525
4	2.5092	2.4094	3.0764
5	4.0134	3.9195	5.0104
6	4.3579	4.2988	1.0027
7	4.5511	4.4727	1.0134
8	4.8381	4.7495	1.0134
9	6.9300	6.8632	1.0148
10	7.1314	7.0693	1.0

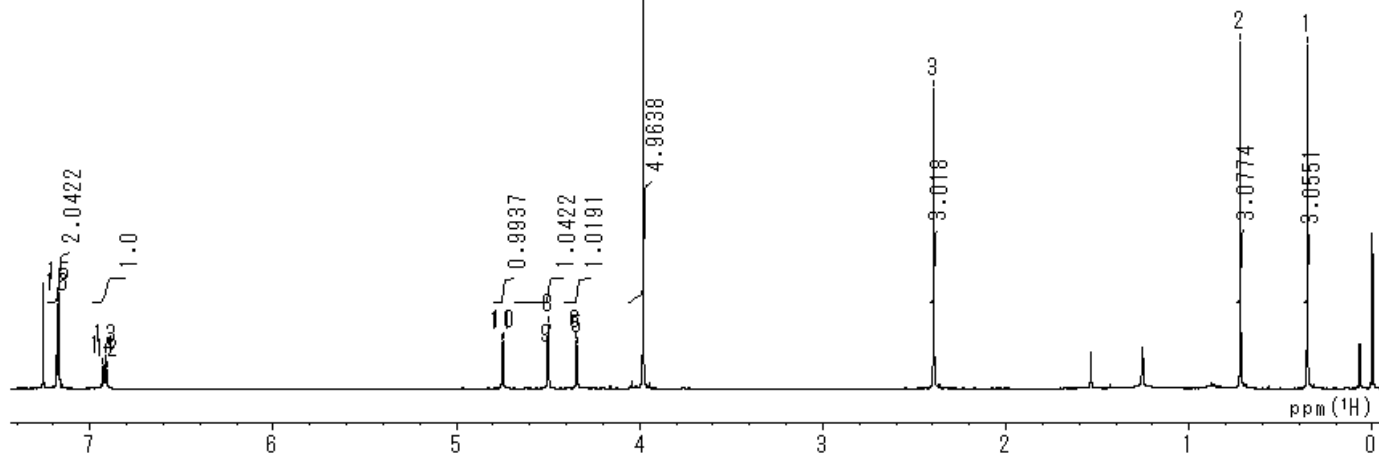
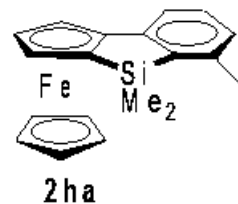


No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height
1	-2.56	14.60	8	70.95	4.74	15	141.70	6.15
2	-1.83	15.27	9	72.32	16.98	16	142.00	5.73
3	19.99	13.43	10	96.16	4.76			
4	20.13	19.58	11	129.77	16.39			
5	66.55	17.42	12	130.71	7.44			
6	68.30	79.37	13	131.62	17.24			
7	69.17	18.10	14	133.48	7.71			



No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height
1	0.35	56.07	8	4.50	10.33	15	7.17	15.70
2	0.72	56.51	9	4.51	5.38	16	7.18	13.91
3	2.39	48.99	10	4.74	7.77			
4	3.98	98.99	11	4.75	7.60			
5	4.34	7.18	12	6.91	3.10			
6	4.35	7.76	13	6.92	5.49			
7	4.50	5.57	14	6.93	3.64			

No.	Start (ppm)	End (ppm)	Integral
1	0.3688	0.3412	3.0551
2	0.7391	0.7030	3.0774
3	2.4167	2.3812	3.018
4	4.0614	3.9262	4.9638
5	4.4094	4.2631	1.0191
6	4.6804	4.4094	1.0422
7	4.7975	4.6804	0.9937
8	6.9864	6.8034	1.0
9	7.2279	7.1108	2.0422



No.	δ /ppm	Height	No.	δ /ppm	Height	No.	δ /ppm	Height
1	-1.80	4.65	8	73.85	5.27	15	149.06	1.85
2	-0.94	4.64	9	95.45	1.59			
3	64.45	4.45	10	116.94	2.13			
4	69.63	3.23	11	121.73	2.37			
5	69.84	23.02	12	126.28	1.05			
6	71.02	4.82	13	132.61	5.05			
7	71.79	1.85	14	146.80	1.58			

